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CONTENTS.

PAGE.
Proceedings ..... (47)–(48)

PAPERS.
The Value of a Bacteriological Examination of Water from a Sanitary Point of View. By E. K. Dunham 591
On the Influence of Vegetable Mold on the Nitrogenous Content of Oats. By H. W. Wiley 605
Notes on the Determination of Insoluble Phosphorus in Iron Ores. By Charles T. Mixer and Howard W. Dubois 614
The Physical Effects of Various Salts and Fertilizer Ingredients upon a Soil as Modifying the Factors which Control Its Supply of Moisture. By J. L. Beeson 620
The Rapid Estimation of Uric Acid in Urine. By E. H. Bartley 649
The Atomic Mass of Tungsten. By Willett Lepley Hardin 657
Obituary 676
NOTE: Hydrolysis of Starch by Acids 679
NEW BOOKS: Traité de Chemie Organique d'aprés les Théories Modernes 680
Books Received 681
Errata 682

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PAPERS ACCEPTED FOR PUBLICATION:

The Exact Estimation of Total Carbohydrates in Acid Hydrolyzed Starch Products. By Geo. W. Rolfe and W. A. Faxon.

The Action of Certain Bodies on the Digestive Ferments. By F. D. Simons.

A Preliminary Thermo-Chemical Study of Iron and Steel. By E. D. Campbell and Firman Thompson.

Further Study of the Influence of Heat Treatment and Carbon upon the Solubility of Phosphorus in Steel. By E. D. Campbell and S. C. Babcock.

Derivatives of Eugenol. By F. J. Pond and F. T. Beers.

The Composition of Humus. By Harry Snyder.

An Electrical Laboratory Stove. By M. D. Sohon.

On the Speed of Reduction of Ferric Alum by Sugar. By J. H. Long.

Method for Collecting and Analyzing Gases in Canned Goods. By Chas. A. Doremus.

The Bibliography of Aluminum. By T. B. Stillman.

Mechanical Arrangement of Fat Extraction Apparatus. By G. J. Volckening.

Early American Chemical Societies. By H. Carrington Bolton.

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THE JOURNAL

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THE VALUE OF A BACTERIOLOGICAL EXAMINATION OF WATER FROM A SANITARY POINT OF VIEW.[1]

BY E. K. DUNHAM.

Received May 12, 1897.

SEVERAL years ago, when connected with the Massachusetts State Board of Health, the author had occasion to make bacteriological examinations of a large number of samples of water, derived from various sources. The method then in use was to mix one cc. of the water with about nine cc. of sterile nutrient gelatin, and to pour the mixture upon sterilized glass plates, where it solidified in a moderately thin layer. These plates were then kept under cover for two, three, or four days, to protect them from dust and from drying, after which they were examined either under the microscope, with a hand lens, or with the unaided eye. The number of colonies that developed on these plates was then recorded.

It appeared to me at that time, 1887, that it was not possible to judge of the quality of a water from the data so obtained. This opinion was supported in a striking manner by observations, of which the following is a good, though somewhat extreme, example. The water supply of one of the towns near Boston was derived from a series of driven wells, consisting of iron pipes forced into the sandy soil. All but one of these wells were connected with a pipe leading to the pump which drove the water into the town reservoir. The remaining well was not connected with the others, but was used for making observations

[1] Read at the Special Meeting of the New York Section, April 23, 1897.

on the level of the ground water. It was kept covered, except when used for that purpose.

I found that the water taken from the tap at the pumping station, after it had passed through the pump, contained two bacteria to the cubic centimeter, *i. e.*, it was practically sterile. Water taken from the observation well contained about 5,000 bacteria to the cubic centimeter.

The water in both cases was from the same source, namely the ground water, but that which passed through the closed pipes was protected from infection, while that from the observation well had been exposed to the entrance of bacteria from the air. The bacteria found in the water from this well were all of the same species, and the inference was plain that, of those bacteria which accidentally gained access to the water, only one species had found the conditions favorable for its indefinite multiplication. There could not be any doubt that the two waters were equally fit for drinking, provided the single species, which was present in such abundance, was unobjectionable. At that time the maximum number of bacteria that was considered permissible in a good water was set at 250; yet this perfectly wholesome water contained twenty times that number.

Similar observations soon led me to the conclusion that a water might contain a large variety of bacterial species without being injurious to health. The water of small brooks flowing from springs in wooded regions frequently contains numerous species of bacteria derived from the air and the banks of the stream, yet there is no reason to suppose that such water is unfit for drinking.

The manner, then in vogue, of interpreting the results of such a bacteriological examination by the plate method appeared to me to be artificial and inadequate, because the accepted standards of purity were based upon quantitative differences. The method itself was not wholly without value, for it appeared possible to gain some insight into the probable bacterial history of a water, by a simple inspection of the plate cultures, prepared from it. Pure waters, originally free from bacteria, but subsequently exposed to the atmosphere, when examined by plate culture, yielded colonies composed of bacteria, which, as a rule, failed to liquefy gelatin and frequently possessed chromogenic

powers. The water accumulating in collecting wells or trenches protected from surface drainage by walls of brick or stone and covered by structures permitting free ventilation, gave plate cultures of this character. The bacteria it contained were derived from the air.

Those waters which had received additions coming in contact with vegetation and the upper strata of the soil, contained the bacillus subtilis, the bacillus mycoides, and the bacillus figurans, all easily recognizable by the characters of the colonies resulting from their growth on gelatin plates. The waters of unpolluted brooks and small streams arising from springs in rural districts contained these bacteria, as well as those coming from the air.

It is doubtful whether any of the waters from larger streams or rivers, which I examined, were free from pollution by either sewage or waste from factories. The plate cultures from such waters revealed a varied flora, and it was not possible to identify, on the plate cultures, the species that I regarded as evidence of the presence of air bacteria and bacteria derived from the soil. It is probable that the bacteria resulting from the pollution of the water were more abundant or grew more rapidly than those from the air and soil and, in consequence, concealed their presence.

Plate cultures made from sewage and those prepared from waters that had certainly received sewage, contained colonies of a yellowish or brownish color, when viewed under the microscope. They were round, oval or lenticular in shape, and usually presented a multicontoured appearance, if the plates were not too crowded. These colonies I now believe to have been those of the common colon bacillus. The practically constant presence of such colonies, on plates from water contaminated with sewage, led me to look upon them as an indication of dangerous pollution.

I think there were good grounds for the opinion I then formed that the mere number and variety of bacteria in a water are of comparatively little significance, but that the presence of certain species might be accepted as indicating that the water had been exposed to certain pretty definite conditions before it was submitted to bacteriological examination, and that a knowledge

of those conditions was of importance to a just estimation of the probable risk of drinking the water.

The chief aim of an examination of water with reference to its fitness for drinking is to learn whether it contains, or is likely in the future to contain, poisonous substances, or the contagia of disease. The detection of mineral poisons falls within the domain of chemistry. The actual isolation of specific bacteria of disease can only be done by bacteriological methods. But in the vast majority of the cases in which an examination of water is required, mineral poisons are not present in notable quantities, nor are pathogenic bacteria so abundant as to be certainly detected by the methods now available. The object of an examination of the water in these cases is to estimate the degree of probability that in some future time the particular water in question may become the carrier of infection. This question practically resolves itself into the detection of pollution with sewage, which may at some time contain dejecta from cases of disease. The usual chemical examination aims at detecting such pollution, and a bacteriological examination may be directed towards the same end. By the former method, the soluble substances, which are abundant in sewage, are estimated. By the latter, the bacteria derived from the intestinal tract and those of putrefaction, which thrive in solutions rich in animal organic matter, are sought, and, if need be, isolated. When sewage is mixed with water, both these methods for its detection are applicable, but it appears to me that the bacteriological test is capable of being the more delicate and precise of the two methods.

An exhaustive bacteriological examination which undertook the isolation of every species present in a given water, and endeavored to trace the way in which each species gained access to the water, would require a much wider and more exact knowledge of the distribution of bacterial species than we at present possess. And even if that knowledge were available, such an examination would require a very protracted study of the water. It appears necessary, therefore, to resort to a few simple procedures which are likely to give the information strictly required for a just conception of the general bacterial

history of the water and to base the judgment of the sanitary value of the water upon the results so obtained.

I will give a brief outline of the methods that appear to me most likely to furnish useful knowledge respecting the wholesomeness of a water from a bacteriological standpoint, assuming that the main questions to be answered are: (1) whether the water has been polluted with sewage, and (2) in case there are many bacteria in the water, whence they were probably derived.

It so happens that most of the bacteria found in the air are strict aerobes, *i. e.*, are incapable of growth, save in the presence of oxygen. We may take advantage of this fact to gain a rough idea of the number of bacteria in the water which owe their presence to aerial contamination. My plan is to prepare four gelatin plates, with one cc. of water on each plate, and to allow two of them to develop in an ordinary moist chamber, the other two being kept in an atmosphere of hydrogen. When those which have been exposed to oxygen are ready for counting, all four plates are examined and the number of colonies estimated. I will give examples of the two sets of observations, illustrating the results obtained by this method.

Experiment I.—Distilled water taken from a demijohn which had been exposed to contamination from the air for at least two weeks, was examined in this way. At the end of two days the plates grown with access of air contained 1,395 colonies. Those grown in hydrogen showed no colonies at all. The latter were then placed in a moist chamber, where they were exposed to oxygen for two days. At the end of this time they contained 1,469 colonies, showing that the bacteria in the water were not *killed* by the hydrogen, but were incapable of growing to any great extent when in an atmosphere of that gas.

Experiment II.—A similar experiment was made with croton water. The plates grown in air contained 135 colonies. Those grown in hydrogen contained 30 colonies, but, after exposure to the air, the number increased to 128 colonies. It seems, therefore, that the croton water contains species that were at least facultative anaerobes, and probably some that were not originally derived from the air.

Those bacteria that are capable of producing specific diseases are nearly all facultative anaerobes, so that it is safe to infer

that the distilled water taken for the first experiment was fit for drinking.

It is probable, from their microscopical appearance, that some of the colonies on the hydrogen plates from the croton water, were those of the proteus vulgaris, one of the bacteria most frequently found in putrefying organic matter, of animal origin.

Although the bacteria, prevalent in the air, are usually dependent upon the presence of oxygen for their multiplication, it must not be assumed that all the strictly aerobic bacteria, found in a water, have been derived from the air. Many of those occurring in the soil are incapable of growing without a supply of free oxygen. This is shown by the following experiment.

Experiment III.—One gram of soil from near the surface of the ground was introduced into a liter of water which had been sterilized by prolonged boiling, and after vigorous shaking, plates were prepared as in the preceding experiments. The plates grown in air contained 38,771 colonies, those grown in hydrogen 534 colonies. The general appearance of the two sets of plates was very different. The air plates contained numerous colonies of mycoides, figurans, and the hay bacillus. The hydrogen plates contained only a slight growth of figurans, visible under the microscope. The hay bacillus and mycoides did not develop on the plates grown in hydrogen.

If we now turn our attention to the results obtained by this method, when sewage is examined, we shall find that the number of facultative bacteria is very much greater in proportion to the number of strict aerobes, than was the case in the experiments with water, contaminated with species from the air or soil.

Experiment IV.—Plates were prepared, each with one cc. of sewage from one of the main sewers of this city. After twenty-four hours the colonies were estimated with the aid of the microscope. The air plates contained an average of 51,516 colonies, the hydrogen plates 49,871, a difference of only 645 in over 50,000.

Experiment V.—One cc. of the same sewage was added to one liter of sterilized distilled water, and with one cc. each, the plates were prepared. Those grown in air contained 260 colonies, those grown in hydrogen 278. In this case the number of colo-

nies on the hydrogen plates was greater than the number on the air plates, a circumstance that need occasion no surprise when we reflect that the sewage contained little masses of suspended matter that would prevent a perfectly uniform mixture with water, and might, therefore, easily cause some of the samples, taken for bacteriological examination, to contain more bacteria than others.

Experiment VI.—The diluted sewage used for the last experiment was allowed to stand at the room temperature for three days and the examination was then repeated. The plates grown in air contained 18,187 colonies; those grown in hydrogen 17,197.

The last three experiments show that a large proportion of the bacteria in sewage are probably facultative anaerobes, and that a considerable dilution of the sewage does not prevent a rapid multiplication of the bacteria it contains. Such a dilution would improve the chemical character of the water, but leaves its bacteriological character unchanged.

A comparison of the results of the six experiments, detailed above, demonstrates that the method used is capable of throwing considerable light on the significance of the bacteria found in a sample of water.

It would not do, however, to leave the consideration of that method without pointing out a possible source of error in the deductions, drawn from the results of these experiments. It might be that there were two sets of bacteria on the plates, one consisting of strict aerobes, and the other of strict anaerobes, and that one or the other of these groups would develop on the plates, according to whether they were exposed to oxygen or not. I believe myself justified in excluding this possibility, on the ground that the characters of the colonies on the hydrogen plates were essentially the same as some of those on the plates grown in the air, both when examined under the microscope and with the unaided eye. The fact that the hydrogen plates, when subsequently exposed to oxygen, contained practically the same number of colonies as those which were originally grown in the presence of oxygen, also tends to exclude the source of error we are considering.

The simple procedure used in the above experiments would not alone suffice to reveal the presence of sewage. We must

gain a more definite idea of the characters of the bacteria in the water, where it is shown to contain facultative anaerobes before we are justified in concluding that they are an indication of sewage contamination.

All sewage that receives human feces contains the bacillus coli communis, or if it does not, has been subjected to germicidal agencies that would also kill pathogenic bacteria, derived from cases of disease. It is fair to assume that ordinary sewage would also contain the common bacteria of putrefaction. We must, therefore, direct our attention to the means of demonstrating the presence or absence of those species in the water under examination.

I am inclined to believe that the best way to accomplish this is the application of the putrefactive test based upon the method proposed by Schardinger in the *Centralblatt für Bacteriologie und Parasitenkunde*, **16**, 833, *1894*.

To about ninety cc. of the water, ten cc. of a ten per cent. pepton, five per cent. salt solution, previously sterilized, are added. The mixture is made in a sterile Erlenmeyer flask, provided with a cotton plug. A strip of paper, impregnated with lead carbonate, is suspended over the mixture and the flask is then placed in the incubator at 37° C. for twenty-four hours. Under these conditions of temperature and nutrition, the colon bacillus and the bacteria of putrefaction readily multiply, and the latter cause the production of hydrogen sulphide, which discolors the lead paper. A pure water will not cause a darkening of the paper, but as it is possible that a water which would not cause infection, either at the time or in the future, might contain putrefactive bacteria, this test alone should not be relied upon to decide whether a water is fit for drinking or not.

In order to detect the presence of the colon bacillus a loopful of the above mixture, after the twenty-four hours of incubation, may be used for the preparation of a series of plate cultures in various degrees of dilution. From these plates there is no difficulty in obtaining pure cultures of that bacillus, which may be used for further cultures made for the purpose of definitely identifying it, and, especially, of distinguishing it from the bacillus equi intestinalis, which appears to be the most common species present in the feces of horses.

This method takes considerable time, and if it be desired to simply prove the absence of the colon bacillus, there is a shorter method which can be employed. It consists in inoculating a series of fermentation tubes, containing nutrient bouillon, to which two per cent. of glucose has been added, with the water under examination, using one cc. of water for each fermentation tube. The tubes are then placed in the incubator. The colon bacillus has the power of causing fermentation with a production of gas when grown in sugar solutions. This gas collects in the upright limb of the fermentation tubes. If no gas is found in any of the tubes, it may be assumed that the colon bacillus was absent. But if gas is found it does not prove that the colon bacillus was present, for other bacteria are capable of decomposing sugar with a production of gas. It then becomes necessary to isolate the bacteria in the fermentation tube with a view to determining the presence of the colon bacillus, a matter of no difficulty.

The procedures which are now outlined constitute those which are thought most likely to throw light upon the sanitary value of a water. Let me next call attention to the results obtained by their employment in the examination of some samples of water.

Experiment VII.—The results obtained from croton water were as follows:

1. Plate cultures grown in air contained 135 colonies.
2. Plates grown in hydrogen contained thirty colonies.
3. The putrefactive test blackened lead paper within twenty-four hours, and emitted a foul, somewhat fecal odor. Plate cultures from the putrefaction flask revealed the presence of the colon bacillus and the bacillus proteus vulgaris.
4. The fermentation test showed a production of gas, and cultures made from the fermentation tubes revealed the colon bacillus.

It seems safe to infer from these results that the croton water had been exposed to pollution with sewage, but that the latter had been greatly diluted, and probably also exposed to contamination from the air and admixture with some surface drainage. The latter inferences are based upon the large proportion of

aerobic bacteria in the water, and of colonies of mycoides and subtilis on the plates developed in the air.

Experiment VIII.—A reservoir water from a town near New York yielded the following results:

1. Plates grown in air contained 2,090 colonies.
2. Plates grown in hydrogen contained 165 colonies.
3. The putrefactive test caused no blackening of the lead paper.
4. The fermentation test showed the production of gas, but cultures prepared from the fermentation tubes failed to reveal the presence of the colon bacillus. There were a few colonies of mycoides on the plates grown in air.

The evidence furnished by these results are in accord with the known facts about this water. They permit the inference that the water had not been contaminated with sewage, and was therefore free from putrefactive and intestinal bacteria, but that it had been exposed to the air and to contact with the upper layer of the soil.

If we accepted the simple enumeration of the bacteria in a water as a guide to a judgment of its purity, we should be erroneously led to consider croton water as purer than this reservoir water, whereas the methods actually employed show the reverse to be the case.

Where the presence of sewage and surface drainage is revealed by these methods, as in the case of the croton water mentioned, we should, in estimating the risk of infection from drinking the water, consider (1) the extent to which the sewage has been diluted, and (2) the dangers incident to the surface drainage.

That the dilution had been considerable is shown by the bacteriological examination, for the number of anaerobic bacteria was small, but the degree of dilution cannot be so accurately gauged by that method as by a chemical examination. Croton water, at the time this bacteriological examination was made, revealed nothing, on chemical examination, which would cause suspicion that it contained sewage. The dilution must, therefore, have been very considerable.

The danger from the surface drainage could only be estimated by a local inspection of the surroundings of the water.

The results of these examinations and the inferences drawn from them are in close agreement with the known facts regarding the croton and reservoir waters, and they tend to confirm the value of the procedures described.

But it does not always happen that the results of chemical and bacteriological examinations are in such close accord. I had occasion at one time to examine the water from a deep artesian well, and found the water practically free from bacteria. The chemical examination showed the presence of large quantities of the ammonias, nitrates, and chlorides, and the chemist's report strongly condemns the water. Local inspection revealed the fact that the fields around the well were used for the disposal of the sewage from a large penal institution in the neighborhood, and that the water from the well was used to supply that institution.

It appears to me, that under these conditions, which had persisted for years, the water might be considered as free from objections so long as the upper portions of the well remained water-tight. For it was evident that the percolation of the sewage through the soil removed the bacteria which it contained. The three modes of investigation reveal the conditions obtaining at the time and also point out the possible future dangers.

It would not do to regard the presence of the colon bacillus as a proof of pollution with sewage without other confirmative evidence. The feces of cattle and other animals contain that bacterium, and it is a pretty widely distributed saprophyte, especially in inhabited regions. The fact that it is found in milk, and, after a day or two, in the intestinal discharges of new-born children, is often cited as proof of its wide distribution. I do not think that too much stress should be given to that evidence when we consider the way in which children are born, and the way in which cows are usually milked. If the colon bacillus is present in a water in considerable quantities, as shown by a series of fermentation tubes, it is very unlikely that it gained access to the water in an innocent way.

When the colon bacillus reaches a water in company with sewage, there is sufficient organic matter of animal origin to furnish it with nourishment, favoring its rapid multiplication. We have had an example of this multiplication of the sewage

bacteria, of which the colon bacillus formed a considerable proportion in Experiment VI. In three days the number of bacteria rose from 260 to 18,187, an increase of nearly 600 per cent.

In order to gain a clearer idea of the conditions under which the colon bacillus would multiply in water, the following three experiments were instituted:

Three sterilized, cotton-plugged flasks each received one liter of distilled water, which was boiled in the flasks for one hour to sterilize it.

Experiment IX.—To one of these flasks one cc. of a filtered suspension of the colon bacillus, in sterilized distilled water, was added. The bacillus had been grown upon agar in order to get an abundant growth with the least admixture of organic matter from the nutrient medium. It was then carefully scraped off the surface of the agar and mixed with the sterilized water. After this the mixture was filtered in order to remove any considerable masses of bacilli not broken up during the mixing. After vigorous shaking the water in the flask contained 42,791 bacilli per cubic centimeter, as shown by plate culture.

The flask was kept at the room temperature, exposed to diffuse daylight. After twenty-four hours the water was again examined, when it was found that the number of bacilli had fallen to fourteen.

Experiment X.—The second flask received, in addition to the colon bacillus, one cc. of nutrient bouillon. After the mixture was made, the water in this flask contained 57,102 bacilli to the cubic centimeter. After twenty-four hours it contained 29,276.

Experiment XI.—The third flask received an addition of one cc. of an infusion of hay, instead of the bouillon. On the first day the water contained 14,030 bacilli. After twenty-four hours the number had fallen to 439.

These three experiments go to show that the colon bacillus requires a considerable quantity of organic matter for its abundant multiplication. Dr. A. P. Hallock kindly made a chemical examination of the water in these three flasks, with the following results:

PARTS IN 100,000.

Flask 1.	Free ammonia	0.00575
	Albuminoid ammonia	0.00175
Flask 2.	Free ammonia	0.03675
	Albuminoid ammonia	0.2672
Flask 3.	Free ammonia	0.0125
	Albuminoid ammonia	0.0008

Numerous experiments have been made by various investigators to learn the behavior of the colon bacillus when introduced into natural waters, both with and without previous sterilization. Their results have, in the main, been the same as those just given for these artificial mixtures. As a rule the number of bacilli decreased, but sometimes it remained about the same, or increased slightly, but not to the same degree as did the number of so-called "water bacteria" in the sample.

It seems to me that these observations support the belief that the colon bacilli, which accidentally gained entrance to a water, without an associated pollution with sewage, would fail to multiply to any great extent, and that they would certainly very rarely lead to erroneous inferences from the results of a bacteriological examination. Neither the colon bacillus nor the widely distributed proteus vulgaris cause the evolution of hydrogen sulphide when they are present in water submitted to the putrefactive test. So that an accidental presence of those bacteria would not be bacteriologically equivalent to admixture with sewage.

In this connection it would be of interest to know about the viability of the colon bacillus when subjected to desiccation and light.

The following experiments have a bearing upon this question:

Small threads of sterilized silk were moistened with bouillon cultures of the colon bacillus and then dried in a desiccator over sulphuric acid.

Experiment XII.—Bouillon culture grown in the incubator. Threads exposed to diffuse daylight. The bacillus failed to develop when the threads were placed in fresh bouillon after thirteen days of desiccation.

Experiment XIII.—Bouillon culture grown at the room temperature. Threads exposed to diffuse daylight. Bacillus dead after twenty days.

Experiment XIV.— Bouillon culture grown in incubator. Threads exposed to sunlight. Bacilli dead after six days.

Experiment XV.—Bouillon culture grown at the room temperature. Threads exposed to sunlight. Bacilli dead after ten days.

Similar experiments made with threads moistened with a suspension of human feces, gave the following results:

Experiment XVI.—When exposed to drying over sulphuric acid *in vacuo*, or under ordinary atmospheric pressure, and when exposed to diffuse daylight or direct sunlight, these threads all produced a distinct growth in bouillon after thirty-four days, when the observations were discontinued.

It therefore appears that the viability of the colon bacillus depends upon the conditions under which it is placed. There is apparently no danger of its speedy death when it is associated with fecal matter.

Experience shows that many natural waters, which might readily have received small quantities of the colon bacillus from dust or the surface of the ground, do not contain it in sufficient abundance for its detection by the methods described. This experience is in harmony with the results of the experiments here recorded.

It is, of course, conceivable that a good water might contain adventitious colon bacilli, and this possibility should be borne in mind when conclusions are drawn from the results of a bacteriological examination. It is not probable, however, that such a water would contain a large proportion of anaerobic bacteria, or give a positive outcome to the putrefactive test. If the colon bacillus appeared in considerable quantities in a water, as the result, for example, of drainage from barn-yards, it seems to me that it would indicate an objectionable pollution, even though it were no sign of the presence of human excreta. The author believes, therefore, that the possible conditions which might lead to erroneous inferences from the results of the bacteriological methods of water examination here described, do not seriously invalidate the conclusion that the plan offered is better calculated to give a just estimate of the fitness of a water for drinking purposes than the methods in more common use, and

that they are likely to be of considerable service in a sanitary examination of water.

It is hoped that those who are interested in the subject will put these methods to a practical test in order that their true value may be ascertained, through the experience resulting from their extensive employment.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. NO. 29.]

ON THE INFLUENCE OF VEGETABLE MOLD ON THE NITROGENOUS CONTENT OF OATS.

BY H. W. WILEY.

Received June 7, 1897.

IN growing oats in pots containing vegetable soils from Florida, I noticed that the content of nitrogen in the product was much greater than in oats grown in common soils under the same cultural and climatic conditions. Previous to the beginning of the experiments described below I had noticed a peculiar condition of sugar-cane grown in Florida, on what is there known as muck soils. These soils are composed of vegetable mold, produced under the water in shallow lakes and along the banks of streams. A full description of these soils may be found in my paper on the "Muck Soils of Florida," published in Agricultural Science, 7, 106.

The condition referred to in the sugar-cane was manifested by a brownish color in the juice, which was extremely persistent, affecting even the color of the nearly pure sugar made therefrom. From the character of this coloration there is no doubt of its being due to an actual absorption by the growing sugar-cane of some of the components of the vegetable soil or humus. The fact that plants, under certain conditions, have the faculty of absorbing humus has been subsequently confirmed by the experiments of Snyder.[1] The vegetable soils in which the oats were grown contain in the air-dried state over eighty per cent. of organic matter and less than ten per cent. of sand and other mineral ingredients. The composition of four samples is shown in the following table:

[1] Bull. No. 41, Agricultural Experiment Station of Minnesota.

	Laboratory number.			
	13747	13748	13749	13750
	Per cent.	Per cent.	Per cent.	Per cent.
Moisture	10.30	11.52	8.84	9.35
Organic matter and combined water	83.30	82.21	82.77	83.72
Total nitrogen	2.54	2.59	2.76	2.68
Albuminoid nitrogen	2.44	2.37	2.73	2.52
Amid nitrogen	0.10	0.22	0.03	0.16
Nitrogen as nitrates and ammonia salts	0.03752	0.07952	0.05600	0.08120
Nitrogen as ammonia salts	0.03698	0.05600	0.03510	0.03360
Nitrogen as nitrates	0.00054	0.02352	0.02090	0.04760

Sample No. 13,747 is a virgin soil from the best muck land on the Department Experiment Station near Narcoossee, Florida.

No. 13,748 is from the poorest virgin soil, sample No. 13,749 from a cultivated plot producing good sugar-cane, and No. 13,750 from a cultivated plot where cane failed to grow.

In the mineral constituents of the soil the following quantities of potash and phosphoric acid were found.

	13747	13748	13749	13750
Per cent. of moisture in air-dried material	10.30	11.52	8.84	9.35
Loss on ignition	92.87	92.91	90.80	92.36
Mineral matter[1]	7.13	7.09	9.20	7.64
Potash[1]	0.056	0.057	0.055	0.055
Phosphorus pentoxide[1]	0.066	0.057	0.088	0.173

It is seen from the above data that the soils are deficient both in potash and phosphoric acid, containing generally only about 0.05 per cent of these ingredients except in one instance, where the percentage of phosphoric acid reached almost 0.2. While the data show the almost entire absence of potash, yet the cultures in pot experiments have demonstrated the fact that these soils respond more promptly to treatment with a phosphatic fertilizer than any other, and that they are capable of acting upon the finely ground mineral phosphates of Florida in a manner which makes them easily available to the growing crop.

The soil from the best muck land was found to be entirely free of nitrifying ferments, a culture seeded with it showing no nitrification after forty days. The practical absence of nitric acid in the air-dried sample is therefore not surprising. On the other hand, the molds which produce ammonia in an acid soil appeared to be fairly active. On these soils the oats obtained in 1895 and 1896 were grown. It seems probable from the data

[1] Per cent. on dry material.

obtained that the two samples from the best and poorest soils were interchanged before reaching the laboratory. The crop secured in 1894 was grown on other soils, obtained from the same fields and entirely like those described above in every particular.

The experiments made in 1894 were of a preliminary nature and had for their object a study of the conditions of growth of oats and other crops, with a view to more systematic experiments subsequently. The analytical data relating to the nitrogen in those crops, however, are of so much interest as to demand a rather detailed discussion.

The pots used in the 1894 experiments were made of clay, with perforated bottoms. They were painted with black asphalt paint within and with a white lead paint without. They were thirty cm. in diameter and thirty-seven cm. deep. The bottom of each pot was covered with broken stone and the well mixed vegetable soil placed over this until the pot was full.

STATEMENT SHOWING THE AMOUNT AND KIND OF FERTILIZER ADDED TO EACH POT.

No. of pot.	Fertilizer used.
1	None.
2	36 grams lime mixed with soil.
3	3.6 " K_2SO_4 mixed with upper 6 inches of soil.
4	5.4 " Florida phosphate mixed with upper 6" soil.
5	5.4 " " " " " " 6" "
6	5.4 " slag " " " " 6" "
7	5.4 " superphosphate " " " 6" "
8	3.6 " $(NH_4)_2SO_4$.
9	3.6 " K_2SO_4, 3.6 grams $(NH_4)_2SO_4$; 5.4 grams Florida phosphate.
10	36 " lime; 5.4 grams Florida phosphate.
11	36 " " 3.6 grams K_2SO_4.
12	5.4 " Florida phosphate; 3.6 grams K_2SO_4.
13	5.4 " superphosphate; 3.6 grams K_2SO_4.
14	None.
15	36 " lime
16	3.6 " K_2SO_4.
17	5.4 " Florida phosphate.
18	5.4 " slag phosphate.
19	5.4 " superphosphate.
20	3.6 " $(NH_4)_2SO_4$.
21	5.4 " slag phosphate; 3.6 grams K_2SO_4.
22	36 " lime; 5.4 grams $NaNO_3$.
23	None.
24	36 " lime; 5.4 grams Florida phosphate; 3.6 grams K_2SO_4; 3.6 grams $(NH_4)_2SO_4$.
25	5.4 " $NaNO_3$.
26	36 " lime; 3.6 grams H_2SO_4; 5.4 grams superphosphate.

Nitrogen in the Crop.—The weight of the crop produced and the percentage of nitrogen in the roots, straw, and grain, respectively, are given below. In this connection attention should be called to the fact that, in some instances, a few of the grains were carried off by the sparrows in spite of the watchfulness of the attendant.

TABLE SHOWING WEIGHT OF CROP FROM EACH POT AND QUANTITY OF NITROGEN IN ROOTS, STRAW, AND GRAIN.

Pot No.	Weight of roots.	Nitrogen in roots.	Weight of straw.	Nitrogen in straw.	Weight of grains and chaff.	Nitrogen in grains and chaff.	Average per cent. nitrogen in grains and straw. Crop 1894.
	Grams.	Per cent.	Grams.	Per cent.	Grams.	Per cent.	
1	4.920	1.82	15.512	2.05	1.530	2.69	2.10
2	2.970	1.62	15.070	2.02	3.120	2.75	2.15
3	4.450	1.79	13.250	2.13	1.510	2.75	2.21
4	8.860	1.34	36.010	1.29	2.160	2.58	1.36
5	6.560	1.29	36.320	1.34	4.020	2.69	1.47
6	6.820	1.29	35.100	1.12	5.920	2.52	1.32
7	10.350	1.23	32.470	1.26	3.850	2.55	1.40
8	5.670	1.74	14.760	2.26	0.770	2.24	2.25
9	8.850	1.68	43.530	1.85	9.430	2.80	1.85
10	6.680	1.79	17.920	2.29	1.620	2.80	2.83
11	5.280	1.82	16.530	2.18	1.460	2.69	2.22
12	7.370	1.23	38.150	1.15	3.870	2.46	1.27
13	7.150	1.06	44.150	1.11	6.560	2.41	1.27
14	1.520	1.57	4.330	2.24	0.760	2.58	2.29
15	1.400	1.79	6.080	2.69	0.380	2.58	2.68
16	0.750	1.68	2.070	2.21	0.300	2.52	2.25
17	6.100	1.18	34.830	1.40	2.530	2.69	1.49
18	7.150	1.46	32.650	1.47	2.170	2.58	1.54
19	6.030	1.34	33.230	1.75	2.370	2.75	1.82
20	1.260	1.90	3.520	2.63	0.320	2.80	2.64
21	5.710	1.12	32.980	1.46	1.720	2.46	1.53
22	1.860	1.79	5.830	2.63	1.370	2.58	2.62
23	1.430	1.68	3.880	2.52	0.420	2.46	2.51
24	3.230	1.85	6.320	2.69	1.530	2.46	2.65
25	1.780	1.85	4.530	2.69	0.920	2.80	2.71
26	4.870	1.74	13.270	2.69	3.080	3.14	2.77
Averages,		1.56		1.97		2.63	2.02

The surprisingly high content of nitrogen in all parts of the crop is forcibly shown by the above data. In the unfertilized soils, where the weight of the crop was a minimum, the content of nitrogen is almost uniformly higher than in the fertilized samples, though of course the total weight of nitrogen entering the

crop is much less. The remarkable effect of phosphatic fertilizers in diminishing the percentage of nitrogen is strikingly shown in Nos. 4, 5, 6, 7, 12, 13, 17, 18, and 21. When the phosphate was applied in connection with nitrogenous fertilizers the reduction in the percentage of nitrogen was not so marked, as is shown by Nos. 9, 24, and 26. The data show that in these soils a phosphate is the only required fertilizer, and that it works equally well in each of the three forms in which it was used. In other words, these vegetable soils permit of the easy absorption of the finely ground phosphates without previous treatment with sulphuric acid.

The mean percentages of nitrogen in the three parts of the crop are very high, and this is especially the case in the straw and grain. In this connection it should be mentioned that the grains were ground and prepared for analysis without removing the chaff.

These results were so interesting that it was deemed advisable to repeat the experiments with fresh samples of the vegetable soil. Accordingly, in 1895, twelve pots were filled with vegetable soil, representing four different characters of soil, resembling, in their chemical analyses, the soils already mentioned. Since the roots of the oats crop are never harvested, it was deemed sufficient to confine the examination for nitrogen to the straw and grains. To facilitate the work the straw and grains were ground together so that one analysis was made to do for both. The fertilization of the pots is shown by the following tabular statement:

No. of pot.	
15	Blank.
17	Phosphatic slag.
24	Florida phosphate rock.
26	Blank.
29	Acid phosphate.
18	" "
23	Blank.
7	Phosphatic slag.
28	" "
25	Florida phosphate.
6	" "
16	" "
5	Blank.

The weights harvested from each pot, and the percentages of nitrogen in the straw and grains combined are shown in the following table:

OATS.

Florida soil, 1895.

Pot No.	No.	Weight of crop. Grams.	Nitrogen. Per cent.
15	14,439	14.70	1.82
17	14,440	56.70	2.20
24	14,441	69.50	1.53
24	14,442	37.20	0.90
26	14,443	55.80	1.01
27	14,444	47.20	0.98
29	14,445	53.30	0.95
18	14,449	52.03	1.92
23	14,450	29.30	1.03
7	14,451	51.41	1.05
28	14,452	54.55	0.72
25	14,461	40.71	0.72
6	14,502	37.89	0.92
16	14,503	52.99	2.12
5	14,504	5.59	1.37

While the percentage of nitrogen is not nearly so high as in the results previously given, yet in many instances it is quite excessive. This is particularly so with Nos. 16 and 17, both of which had received phosphatic manures, the nitrogen in these samples being greater than in the unfertilized samples, in which the crop was almost a total failure. The effects of the phosphatic fertilizers, noticed in the first year's experiments, of diminishing the percentage of nitrogen, are not verified by the experiments made in 1895.

Experiments made in 1896.—Experiments made with the Florida vegetable soils were repeated in 1896 with a larger pot, made of metal, containing nearly twice as much soil as in the pots used in the previous years, but with no increase in superficial area. The soils in 1896 were not fertilized, but the character of the fertilizer carried over from the previous year is given in the subjoined table. The pots for 1896 being larger, were filled from two or more pots of the year previous, but the soil received no further fertilization. Any effect of fertilizer, therefore, which will be noticed in the crop is due to the continuous effect of the fertilizer from the previous year.

The character of the soil in each pot and the nature of the fertilizer residual from the amount added the previous year are shown in the following tabulation :

Pots 135, 136, 137, and 138 were filled with the Florida soil, No. 13,747.

Pots 139, 140, 141, and 142 contain soil No. 13,748.

Pot 143 contains soil No. 13,749.

Pots 144, 145, and 146 contain soil No. 13,750.

The residual fertilization of each of the pots is as follows :

No. of pot.	Character of fertilizer.
135	No fertilizer.
136	Florida phosphate.
137	Phosphatic slag.
138	Acid phosphate.
139	No fertilizer.
140	Florida phosphate.
141	Phosphatic slag.
142	Acid phosphate.
143	Florida phosphate.
144	No fertilizer.
145	Florida phosphate.
146	Phosphatic slag and acid phosphate.

The weight of the crop harvested from each pot and the percentage of nitrogen in the straw and grain combined are given in the following table :

OATS.

Florida soil, 1896.

Pot No.	No.	Weight of crop. Grams.	Nitrogen. Per cent.
135	15,515	27.4	1.71
136	15,516	46.6	1.53
137	95,517	33.8	1.09
138	15,518	35.6	1.23
139	15,519	19.9	1.98
140	15,520	46.1	1.81
141	15,521	51.6	1.75
142	15,522	52.2	1.79
143	15,523	39.5	1.11
144	15,524	38.7	1.01
145	15,525	37.1	0.97
146	15,526	33.4	1.06

The above data show that the unfertilized soils had been

improved by two years of cultivation, so that they produced nearly as large a crop, at least in one instance, as those which had received fertilizers in the previous year. In two instances, *viz.*, pots 135 and 139, the unfertilized crop being small, showed the highest percentage of nitrogen, while in a third instance, *viz.*, 144, the percentage of nitrogen was quite low, but in this case the crop was quite large. In general, therefore, the data show that the addition of phosphatic fertilizers, as in the first year's experiments, tended to diminish the actual percentage of nitrogen in the crop harvested.

For the purpose of comparison, the nitrogen was determined in the straw and grains of oats grown in ordinary agricultural soils from six different states in 1895 and 1896. These samples were selected without reference to the content of nitrogen which they contained, but indiscriminately, for the purpose of securing samples of representative or typical soils. The average content of nitrogen in fourteen samples of straw and oats grown in 1895 in common agricultural soils from Missouri, Michigan, Illinois, Wisconsin, Maryland, and the District of Columbia was 1.13 per cent. These crops were grown at the experimental vegetation house of the Division of Chemistry under exactly the same conditions as attended the growing of the crops on the Florida soils, fourteen samples of which the same year showed an average content of 1.30 per cent. of nitrogen in the straw and grains. In 1896 the average content of nitrogen in twelve samples of oats grown on the representative agricultural soils from Missouri, Michigan, Illinois, Wisconsin, Maryland, and the District of Columbia was 1.04 per cent., while in twelve samples grown under identical conditions on the vegetable Florida soils the average content of nitrogen was 1.42 per cent. Thus, leaving out of the comparison altogether the data obtained from the analysis of the 1894 crop, it is seen that in the case of oats the content of nitrogen in the grain and straw is very much larger when the crop is grown on the vegetable mold than when it is grown on the ordinary agricultural soils from different parts of the country. When it is remembered that these vegetable soils are extremely rich in nitrogen, as was shown in the analyses given in the first instance, and when it is further considered that they are quite deficient in nitrifying ferments, it is fair to con-

clude that at least a portion of this excess of nitrogen which they contain is assimilated directly from the vegetable mold without previous oxidation to nitric acid.

Relative Proportions of Proteid and Non-Proteid Nitrogen.—The relative distribution of the nitrogen in the various samples between the proteid and non-proteid forms is also a subject of interest. In the crop of 1894 the average percentage of nitrogen in the whole crop was 2.02. The quantity of material at hand did not permit of the separation of the nitrogen in all the samples. This separation, however, was accomplished in thirty-one instances, *viz.*, in fourteen samples of the roots, eleven samples of the straw, and six samples of the oats and chaff. The average percentage of total and amid nitrogen in the classes named was as follows :

	Roots. Per cent.	Straw. Per cent.	Oats and chaff. Per cent.
Total nitrogen (average).....	1.45	1.99	2.63
Amid " "	0.32	0.70	0.35

In the 1895 crop the separation was accomplished in fifteen samples of straw and grain together. The average percentage of total nitrogen in the samples examined was 1.27, and of amid nitrogen 0.44.

In the crop for 1895 the separation was accomplished in eleven instances, and the average percentage of total nitrogen found was 1.45, and the percentage of amid nitrogen was 0.29.

Comparing these relative percentages of amid and proteid nitrogen with crops grown in ordinary soils, it is found that in twelve samples grown in miscellaneous soils from different parts of the country in 1895 the percentage of total nitrogen was 1.15, and of amid nitrogen was 0.24, and in 1896, in fifteen instances of crops grown on miscellaneous agricultural soils from different parts of the country, the percentage of total nitrogen was 1.18, and of amid nitrogen 0.20.

It will be seen from the above data that the content of amid nitrogen in the crops grown in the vegetable soils was abnormally high, and that the content of proteid nitrogen in the crops grown on the vegetable soils was fairly comparable with the content of proteid nitrogen in the crops grown on miscellaneous soils. This is another important observation to be considered

in connection with the nitrogen content of the crop, and it is fair to infer from the data collected during the three seasons that the tendency of the vegetable soil rich in nitrogen is to increase the total nitrogen content of oats grown therein, but that this increase is chiefly due to the content of non-proteid nitrogen.

CONCLUSIONS.

(1.) Oats grown upon humus soils contain about twenty-five per cent. more nitrogen than those which are grown upon ordinary agricultural soils.

(2.) The increase in the amount of nitrogen noted above is found chiefly in the amid, and not in the proteid nitrogen.

(3.) Fertilization of humus soils, such as were used in these experiments with potash and nitrogenous fertilizers, did not have any appreciable effect upon the quantity of the crop.

(4.) The use of phosphatic fertilizers in connection with these humus soils greatly increases the quantity of the crop and diminishes the percentage of nitrogen contained therein. This diminution in the percentage of nitrogen appears to have resulted chiefly from the increase in the crop, and not to any deleterious influence of the phosphatic fertilizer.

(5.) The three forms of phosphatic fertilizer employed, *viz.*, finely ground soft Florida phosphate, phosphatic slag, and acid phosphate exert an almost identical influence in increasing the quantity of the crop.

(6.) Oats grown upon humus soils absorb directly therefrom a portion of the nitrogen contained therein, chiefly in the form of non-proteid nitrogen.

My thanks are due Mr. T. C. Trescot for his valuable assistance in the nitrogen determinations.

NOTES ON THE DETERMINATION OF INSOLUBLE PHOSPHORUS IN IRON ORES.[1]

BY CHARLES T. MIXER AND HOWARD W. DUBOIS.

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ONLY within the past few years have chemists recognized the importance of the fact, that comparatively large amounts of phosphorus may occur in the siliceous residue left

[1] Read at the Chicago Meeting, 1897, of the A. I. M. E.

from the acid treatment of iron ores. We know of one case in which an ore contained about three times as much phosphorus in the insoluble as in the soluble form. It was disposed of at a premium, as an exceptionally high grade Bessemer ore containing 0.010 per cent. of soluble phosphorus, while the insoluble phosphorus brought the total amount up to 0.040 per cent.

The magnetite and the specular hematite of the Lake Superior districts, and the fine ores of the Mesabi range, as a rule, contain very small amounts of insoluble phosphorus. But the mining of the soft hematites and the progressive lowering of the phosphorus limit in a strictly Bessemer ore, have combined to make the determination of insoluble phosphorus one of the routine requirements in all analyses of Bessemer ores.

The insoluble phosphorus is understood to be that phosphorus which cannot be extracted by boiling hydrochloric acid of 1.10 specific gravity. The time given for the extraction of the soluble phosphorus will vary, of course, according to the nature of the ore. In ordinary practice the boiling is continued until the residue is white, or only very slightly tinged with ferric oxide. This ordinarily takes from half an hour to an hour. The prolonged boiling of ores known to contain considerable quantities of insoluble phosphorus has failed to extract any appreciable amount of additional phosphorus. Very fine grinding and subsequent sifting through bolting-cloth, has not increased the extraction. These statements represent the result of experiments carried out to test the opinions of a few chemists, who have maintained that such operations would materially increase the solubility of the phosphorus, generally supposed to be insoluble. The determination of this insoluble phosphorus in laboratories required to make a large number of analyses of ores daily, has added a considerable burden to the ordinary routine work.

The current practice in the treatment of the residue remaining from the acid solution of the ore, in order to transform the phosphorus into soluble form, is to fuse the siliceous residue with sodium carbonate in platinum crucibles, dissolve the fused mass in weak hydrochloric acid and evaporate to dryness to dehydrate the silica. The sodium phosphate is then extracted with weak hydrochloric acid and treated in the usual way for obtain-

ing the precipitate of ammonium phosphomolybdate. This operation requires considerable time and manipulation, and involves the introduction of sodium salts, which sometimes prove unfavorable to the obtaining of a pure precipitate of ammonium phosphomolybdate.

The practice of fusing the ore direct with sodium carbonate, and thus extracting the total phosphorus, requires larger platinum crucibles, and would not be practicable where so many determinations have to be carried on simultaneously, as in the case under consideration.

Hydrofluoric acid has been used to dissolve the insoluble residue, but care has to be taken to evaporate the excess of acid employed if the solution is to be subsequently placed in glass beakers.

Since there has been such increased demand for siliceous ores to mix with the low silica ores of the Mesabi range, chemists have been more than ever annoyed with the determination of insoluble phosphorus, as the increased amount of siliceous matter in the residue has required for fusion proportionately more sodium carbonate, heat, time, and patience.

For this reason we began a series of experiments with the purpose of finding a more rapid and convenient method of determining either the total phosphorus or the insoluble phosphorus by itself.

In the first experiment the ore was intimately mixed with less than an equal bulk of sodium carbonate, and then subjected to a red heat in a platinum crucible, the idea being to convert all the phosphorus into sodium phosphate, without using sufficient sodium carbonate to make a liquid fusion. The results were encouraging. The calcined mixture of ore and sodium carbonate are readily freed from the crucible and easily broken up by the pressure of a glass rod in the beaker. The mass was then boiled in some cases with water alone, and in other cases with weak acids, and the total phosphorus was quickly extracted from many ores containing considerable amounts of insoluble phosphorus. The main objection to this method was encountered, however, when the siliceous ores were treated by it. In such cases, owing to the large amount of siliceous residue, no matter how little sodium carbonate was used, it was difficult to prevent

a partial fusion, forming silicate of sodium, and thus making it hard to remove the calcined mass from the crucible.

Calcined magnesia was next tried as a base to combine with the insoluble phosphorus, and excellent results were obtained, no trouble being experienced with the fusion of the large silicious residues. It was, however, somewhat surprising that the magnesia acted so readily in extracting the phosphorus.

In the experiments next made the ore was calcined without the admixture of any base, and after this operation it was treated in the usual way with hydrochloric acid, when it was found that the total phosphorus had been extracted. This treatment was successful with most of the ores tried, but had the disadvantage of rendering the ferric oxide less readily soluble, and thus increasing the time required for the subsequent solution.

Applying this idea of simple ignition to the insoluble residues only, it was found that all the insoluble phosphorus could be thus converted into the soluble form, and a very simple practical method was thus established.

Very recently our attention has been called to the fact that Mr. Lychenheim[1] and Mr. Norris[2] had come to the same conclusion in the determination of phosphorus in coal and coke—namely, that fusion can be dispensed with and simple ignition substituted. Mr. Lychenheim has also informed the authors that he has found it to be perfectly satisfactory in the case of ores.

The details of our practice are as follows: About one and a half grams of ore are dissolved in a No. 3 beaker with twenty-five cc. of hydrochloric acid, 1.10 specific gravity. When the ore is dissolved, the excess of acid is evaporated until the solution begins to assume a syrupy consistency. It is then diluted with water and filtered into an Erlenmeyer flask, and the filter-paper and residue are placed in a platinum crucible and ignited. When the paper is burned off the residue is broken up with a platinum rod and ignited at a red heat for a couple of minutes, when it is removed and placed in a beaker for solution. Water is added, together with a few drops of hydrochloric or nitric acid, and the solution is brought to a gentle boil for about five minutes. It is then filtered into the flask containing the soluble

[1] A. I. M. E., 24, 66.
[2] *Ibid*, 24, 862.

phosphorus (or into another flask, in case it is to be determined separately)[1], neutralized with ammonia, and precipitated as ammonium phosphomolybdate. The latter precipitate is titrated according to Handy's modification of the sodium hydroxide method.

This method having been found by many tests to give perfectly reliable results, has been in use in our laboratory for more than a year. The following table exhibits a few of the many analyses made by us to satisfy ourselves as to the accuracy of the method.

In order to obtain some general idea of the nature of the base, which was combined with the phosphorus in the insoluble form, we made the following partial analysis of the insoluble residue from the hydrochloric acid treatment.

After drying the residue at 100° C., it was subjected to ignition in a platinum crucible for five minutes:

	Per cent.
Loss on ignition	5.05
Loss due to extraction by acid*	16.25

The residue from the above treatment contained, in percentages of the original residue:

	Per cent.
SiO_2	74.25
Al_2O_3	2.70
CaO	1.37

TABLE OF PHOSPHORUS DETERMINATIONS.

Method A.—Solution of ore and fusion of residue with sodium carbonate (old standard method).

Method B.—Solution of ore and ignition of residue without flux (proposed method).

Method C.—Ignition of ore without flux, and subsequent solution, determining total phosphorus.

[1] It has been found that it is better to determine separately the soluble and insoluble phosphorus. Otherwise a too dilute solution is liable to be obtained for the precipitation.

	Name of ore.	Soluble phosphorus.	Insoluble phosphorus.	Total phosphorus.	Method.
1.	Winthrop[1]	0.051	0.008	0.059	A.
	"	0.051	0.008	0.059	B.
2.	"	0.039	0.008	0.047	A.
	"	0.039	0.008	0.047	B.
3.	"	0.054	0.014	0.068	A.
	"	0.052	0.015	0.067	B.
	"	....	....	0.067	C.
4.	"	0.051	0.008	0.059	A.
	"	....	....	0.058	C.
5.	Cambria	0.052	0.004	0.056	A.
	"	0.053	0.003	0.056	B.
6.	Lillie	0.065	0.006	0.071	A.
	"	0.065	0.007	0.072	B.
7.	Lake Superior	0.021	0.006	0.027	A.
	"	0.020	0.006	0.026	B.
8.	"	0.112	0.022	0.134	A.
	"	....	....	0.135	C.
9.	Salisbury	0.058	0.009	0.067	A.
	"	0.058	0.010	0.068	B.
10.	"	0.028	0.019	0.047	A.
	"	0.028	0.019	0.047	B.
11.	"	0.046	0.006	0.052	A.
	"	0.046	0.006	0.052	B.
12.	Cleveland Hematite	0.022	0.015	0.037	A.
	" "	0.022	0.016	0.038	B.
	" "	0.021	0.016	0.037	B.
	" "	....	....	0.038	C.

The solution (marked *) from the ignited residue contained in percentages of the original residue:

	Per cent.
Al_2O_3	9.55
CaO	0.92
P_2O_5	4.10

From the latter analysis it would appear that the greater part, if not all, of the phosphorus was combined with the alumina.

The conversion of the insoluble phosphorus into the soluble form by simple ignition is a matter of some theoretical interest. The formation of a more soluble phosphate under such conditions certainly does not appear probable. Possibly the method proposed by Berzelius[2] for the decomposition of phosphates, by means of silica and sodium carbonate, may involve a reaction somewhat similar to that which we have here under consideration.

[1] Nos. 1, 2, 3, and 4 are silicious ores.

[2] Fresenius, 6th German edition, 1, 416.

[CONTRIBUTION FROM THE LABORATORY OF BETHEL COLLEGE, RUSSELLVILLE, KY.]

THE PHYSICAL EFFECTS OF VARIOUS SALTS AND FERTILIZER INGREDIENTS UPON A SOIL AS MODIFYING THE FACTORS WHICH CONTROL ITS SUPPLY OF MOISTURE.

BY J. L. BEESON.

Received June 4, 1897.

UPON making a comparative study of the physical properties of the Maryland soils, Milton Whitney has shown that the texture of the soil, or size of the soil particles, controls in the main the amount of moisture that each type of soil will maintain; and, therefore, determines the kind of crops best suited to each.

For early vegetables, where quick maturity rather than yield per acre is the desideratum, a large-grained, loose soil, containing from three to five per cent. of clay, which will maintain about six to eight per cent. of moisture, is best adapted. For a crop requiring a long period of growth, and when yield is an important item, the loose-grained soil will not do, but a fine-grained soil, containing a large percentage of clay, and which will maintain a high percentage of moisture, will be required. Upon this basis of the texture of the various types of soil in the state, the amounts of moisture which each will maintain, and the kinds of crops growing thereon, he has ascertained with considerable accuracy what crops are best adapted to each type of soil in the state. He has suggested that it is possible, by changing the potential on the surface of the soil grains, to pull together or push apart the clay and fine silt grains of a soil, and thus increase or decrease the size of the soil spaces, either by a rearrangement of the particles or by building up or breaking down the soil aggregates.[1] If this can be done, and at reasonable cost, it is clear that it would be of inestimable value to agriculture, for a farmer could thus change the texture of his soil, so as to adapt it to the best growth of that crop or crops which would bring the best price. If this is true, one naturally inquires what compounds will loosen the soil? What make it more compact, and in what degrees? He affirms, also, that "fertilizers have a very marked effect upon the texture of soils * * * that we

[1] Bull. No. 21, Maryland Experiment Station.

have in our common fertilizers and manures very potent means of maintaining or changing the texture of soils, and thereby changing the conditions of moisture and heat which they can maintain for a crop, and that it is through this physical effect of manures and fertilizers in controlling the supply of moisture and heat within a soil under existing climatic conditions that the chief value of fertilizers and manures lies, rather than in the relatively small amount of plant food that they add to the soil."[1]

While this may be the case, Hilgard has pointed out the fact that it has not yet been proved, and claims that Dr. Whitney is maximizing the physical idea, and minimizing the plant-food conception of the use of fertilizers.[2]

Hilgard, in his researches upon the alkali soils of the arid regions and their reclamation, has shown that certain alkaline salts, and especially the neutral sodium carbonate when present in the soil even in very small quantities, so puddles the soil or breaks up the soil aggregates as to render the soil very retentive of moisture and exceedingly difficult to get into and to maintain even in tolerable tilth.

The conversion of the sodium carbonate into the sulphate by the use of gypsum, all but completely restores the soil to normal conditions, when a good crop may be grown. By this means large tracts of alkali lands have already been reclaimed. He also states that upon the edges of the alkali spots, when there is only a medium amount of alkali present, the crops are better than in lands in the same locality free from alkali, owing to the fact that the latter maintain more moisture.

These facts would, it seems to me, answer affirmatively Whitney's suggestion that it is possible so to alter the size or arrangement of the soil particles, in some cases at least, as to make the soil more retentive of moisture. But what salts effect the soil most? which ones build up and which break down the aggregates? and in what degrees? still remain to be answered. Also, do the ordinary fertilizer ingredients as added in the usual quantities in practice and which so handsomely increase the yield, affect appreciably the texture of the soil, and thus the soil's supply of moisture? These questions, it was believed, could quick-

[1] Bull. No. 21, Maryland Experiment Station, pp. 18-19.

[2] Agr. Sci., 6, Nos. 7 and 12.

est and best be answered by studying separately those factors which govern the supply of the soil's moisture in an untreated soil, and then in samples of the same soil to which various salts had been added and incorporated into the soil as in practice. Those factors which govern the storing and maintenance of a supply of soil moisture may be briefly stated as follows: (1) rate of saturation of the soil with water; (2) water-holding capacity; (3) after the soil is full of water, its conservation power (*a*) against the percolation of the water through the soil and therefore out of capillary reach, and (*b*) against the evaporation from the surface; and (4) finally the power of the soil to supply water to the root stratum by capillary action. Comparatively large quantities of various salts, when added to separate samples of a given soil, might be expected to modify appreciably the above-named factors of the soil. What would be the effect if the potassium of the soil were doubled as a chloride, sulphate, nitrate, carbonate, phosphate, etc.? if the lime were doubled as a sulphate, hydroxide, carbonate, etc.? if the magnesium salts? if the various commercial forms of nitrogen and phosphoric acid were doubled? What would be the effect if any *two* of these ingredients were added to the soil at the same time? if any *three* of them were added? What would be the effect of the various kinds of commercial fertilizers upon these factors? Should any of these salts have a marked effect in the quantities used, would it affect these factors appreciably, when added in the usual quantities in practice? While no attempt has been made to answer all of these questions in the work now reported, yet they serve to show the magnitude of the field and the importance of the line of inquiry. In order to deal effectively with the work it was necessary to devise a quick and accurate method of estimating these five factors which govern the soil's supply of moisture. Out of the necessities of the case grew the apparatus described below.

APPARATUS FOR THE ESTIMATION OF THE RATE OF ABSORPTION OF WATER BY SOILS, MAXIMUM AND MINIMUM WATER-HOLDING CAPACITY OF SOILS, RATE OF PERCOLATION OF WATER THROUGH SOILS, RATE OF EVAPORATION FROM SOILS, AND RATE OF CAPILLARY RISE OF WATER IN SOILS.

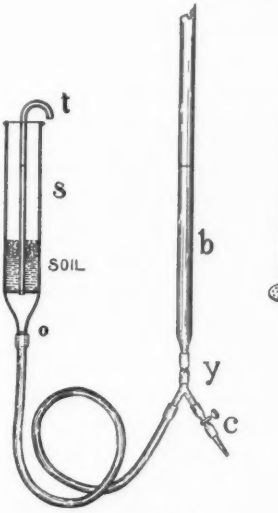


FIG. 1.

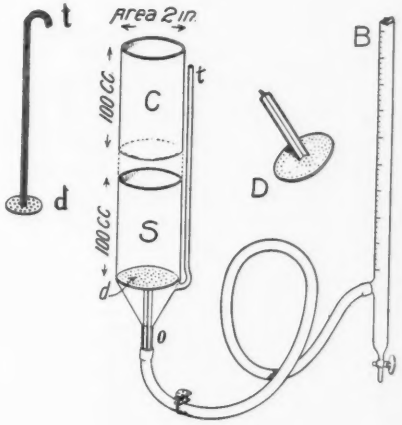


FIG. 2.

Fig. 1 shows the original form of the apparatus, the one with which the results embodied herein were obtained.

Fig. 2 shows the improved apparatus.

Apparatus 1 consists of a filter tube *S*, one and one-half inches in diameter, of such a height that it will hold 100 grams of ordinary soil. It is connected by means of a stout rubber tube to a 100 cc. side-tube burette, or by means of a Y-tube to an ordinary burette. A small glass tube is passed just through the center opening of a perforated copper disk, and fused in. The disk is of such a size that when a filter paper, perforated in the center, is slipped over the glass tube down upon the disk and the edges folded under, it will just fit the soil tube, *S*. The improved apparatus consists of a soil tube, *S*, of two square inches cross-

section, and which holds exactly 100 cc. Where the perforated disk, *D*, lodges there is a mark around *S*, so that the disk may be perfectly adjusted each time the instrument is used. The air tube *t* is on the outside of the soil tube, and enters it just below the perforated disk. The cylinder *C* is joined to *S* by means of a ground joint, and held in place by a wide rubber band. The improved form possesses the following advantages: (1) The soil tube may be stoppered and unstoppered without settling or otherwise disturbing the soil; (2) the minimum water capacity can be readily determined with this instrument, but cannot be with the original one; (3) 100 cc. of the soil are weighed, and that weight taken each time when working with a given soil, and settled in the soil tube to the level. This insures an equal degree of settling in each case, a thing which is very essential in all work for comparative results. The instrument is now filled with water to the zero mark on the neck of the soil tube and on the burette. The pinch-cock at the end of the burette is of the greatest service in bringing the water to the zero mark. The zero mark may be gotten with the paper saturated or with it dry. In the latter case disks of a given size, in which the water capacity has been determined, should be used. The instrument is now ready for use.

Rate of Capillary Rise.—Add either 100 grams or 100 cc. of the soil to the tube *S*, settle by jolting a constant number of times, and raise the burette until the water is touching the bottom of the soil, where it is kept until the stratum of capillary moisture has reached the top of the soil. The time required for this is the rate of capillary rise for this height of soil column, and is obviously a function of size and shape of the capillary spaces.

Rate of Saturation.—After the stratum of capillary moisture has reached the top, the burette is raised until its water-level is one-fourth of an inch above the top of the soil in the tube, where it is maintained. A stratum of maximum saturation, where the spaces in the soil are filled with water, slowly rises, and when it reaches the top and begins to form a surface of water on top of the soil the time is noted. The time required for the capillary ascent in this column of soil, plus that required for the maximum saturation, may be considered the rate of saturation. In

nature the rate of saturation is variable. In low places there will be a pressure from the head of water; on the high places no pressure. So the conditions of the experiment cannot be brought to reproduce those of nature. But for all comparative results the above method is accurate.

Water-Holding Capacity.—Experience has shown that in the case of very fine-grained soils some time is required for a complete saturation, so it is well to leave the water in contact with the soil, with the instrument stoppered, for an hour after the water has made its first appearance on the top of the soil, after which the burette is lowered and allowed to stand until the burette reading is constant. Then the burette is moved so that the water stands at the zero mark on the stem of the soil tube, where the number of cc. absorbed is read, which is also the percentage. Since the specific gravity of soils varies, and since it is desired to know the quantity of water a soil will hold to a given depth, it is better to ascertain these factors in terms of volume. The small tube *t* admits air below the disk as the burette is lowered, so that the water runs out of the soil by gravity alone, as in nature. Then it serves also to indicate the height of the water.

Rate of Percolation.—When the soil is saturated a head of one inch of water is so carefully added on top of the soil that the water is not muddied, and the time required for five cc. to run through is noted. In the improved instrument, a ground glass cylinder is attached, by means of a rubber band, to the top of the soil tube, to which the water is added.

Rate of Evaporation.—After removing the excess of water used in the preceding determination, from the top of the soil, expose the soil tube and contents to evaporation for any desired period of time. Saturate the soil again with water and read off the number of cc. absorbed, which is the amount of evaporation. Owing to the wide variation in temperature, hygrometric state, and motion of the air from hour to hour and from day to day, this method is of very little value for comparative results. But I would recommend it as a method of estimating the total evaporation during a season from a saturated soil, keeping the water in contact with the soil, and the burette and air tube stoppered.

Minimum Water Capacity.—This important factor in the study of the physical properties of the soil may be quickly determined by the use of the improved form of apparatus, as follows: When the soil tube is full and the soil saturated, attach cylinder *C*, and fill it gently with a portion of the same soil, air-dry. Allow it to absorb all the moisture it will, then remove and apply a new portion of the dry soil. Repeat until the dry soil will absorb no more moisture from the soil below. Cut off the soil even with the top of the soil tube *S* by means of a tight thread, then raise the burette and saturate the soil with water, noting the amount absorbed. The difference between this quantity and the maximum water capacity as previously determined, is the minimum water capacity of the soil. It is thus seen that all these six estimations may be rapidly and accurately made upon the same sample of soil, one after the other, without disturbing it in the apparatus.

THE CHARACTER OF THE SOIL EXPERIMENTED WITH.

The soil, obtained from the Louisiana Experiment Station at New Orleans, is dark alluvial deposit from the Mississippi river, and is quite retentive of moisture and exceedingly fertile. Below is given both the chemical and physical analysis of the soil:

CHEMICAL ANALYSIS.

	Per cent.
Insoluble matter	69.900
Potash (K_2O)	0.687
Soda (Na_2O)	0.224
Lime (CaO)	0.882
Magnesia (MgO)	1.288
Iron oxide (Fe_2O_3)	10.380
Alumina (Al_2O_3)	2.190
Phosphoric anhydride	0.127
Nitrogen	0.114
Humus	2.020
S. G. real	2.476
S. G. apparent	1.170

PHYSICAL ANALYSIS.

	Per cent.
Fine gravel, 2-1 mm	0.10
Coarse sand, 1-0.5	0.07
Medium sand, 0.5-0.25 mm	0.14
Fine sand, 0.25-0.1 mm	0.58

	Per cent.
Very fine sand, 0.1-0.05 mm	14.40
Silt, 0.05-0.01 mm	33.03
Fine silt, 0.01-0.005 mm	10.70
Clay, 0.005-0.0001 mm	31.99
Total mineral matter	91.01
Loss at 110° C	5.93
Loss on ignition	3.91
Total	99.85

The chemical analysis was made by one of my pupils, under my supervision, following the method adopted by the Official Chemists. The physical analysis was made by Mr. Matthews, under the supervision of Milton Whitney, Washington. The soil is neither the blackest and heaviest nor the lightest type of the Mississippi bottoms, and probably represents an average rich bottom soil. Several kilos of the soil were obtained dried, ground in a coffee mill, thoroughly air-dried, and then ground so that it would pass through a sieve of forty meshes to the inch. The sample contained about nine per cent. of moisture (8.786 per cent.) which probably represents the minimum moisture of the soil in a drought. The soil was thoroughly mixed, placed in bottles and sealed to prevent any change in moisture content. In the experiments described in this work all results are referred to 100 grams of this air-dried soil. The salts whose effects upon the physical properties of the soil it was proposed to study, were added directly, in a powdered form, to the soil and thoroughly incorporated with it, and the water used in the instrument was rain water, an effort being made to reproduce as near as possible the conditions in nature and in actual practice. The samples of soil, to which the various salts had been added, were kept in sealed bottles. The method of work was to study first the rate of absorption, water capacity, rate of evaporation, rate of percolation, and the capillary action of the untreated soil, then these factors in the samples, to each of which some salt had been added and incorporated. It is not claimed that the soil prepared in this way represents the exact conditions of a soil in nature, and therefore, that it will give the exact rate of saturation, percolation, etc., of a soil in the field. But it will show whether certain salts will so modify the above named factors as to change appreciably the soil's power of maintaining a

supply of moisture. The experiments described in the following pages were made with soil apparatus No. 1, with the soil tube one and one-half inches in diametar using fifty grams of the air-dried soil. No corrections were made for moisture, for this amount of moisture probably represents the soil's minimum moisture in nature.

RATE OF SATURATION.

A study was made of the rate of absorption of water by the soil in each successive interval of time, as follows: Fifty grams of soil were placed in the soil tube and the burette raised so as to bring the water in contact with the soil. It was allowed to remain there for one minute, then the burette was lowered for one minute and the amount absorbed read off. This process was repeated each minute until the absorption became very slow, when the water was allowed to stay in contact with the soil for a longer period. Then the burette was lowered and left down until the reading was constant. Below is given the amount of absorption for each minute of contact:

Time of contact	1st m.	2nd m.	3rd m.	4th m.	5th m.	6th m.	7th m.	7th to 12th m.	12th to 17th m.	17th to 32nd m.	32d to 47th m.	47th to 77th m.	77th to 107th m.
	Per cent.	Per cent.	Per c'nt.	Per c'nt.	Per c't.	Per c'nt.	Per c'nt.	Per c't.	Per cent.	Per cent.	Per cent.	Per cent.	Per c't.
Soil	26.0	10.4	6.6	2.0	0.6	0.4	0.4	0.12	0.025	...[1]	...	...	...
" +0.5 per cent. K_2O as KCl.....	16.2	4.0	2.0	2.0	1.0	1.1	1.1	0.25	0.37	0.17	0.18	0.15	0.05
Soil + 0.5 per cent. K_2O as KNO_3.....	17.8	5.6	2.8	2.2	1.4	1.2	1.2	0.36	0.3	0.2	0.11	0.10	0.06

A stratum of capillary moisture rapidly rose to the top and was slowly followed by one of saturation. These movements, as well as the rate of absorption, were greatly decreased by the presence of the potassium salts. In the cases of both the treated and the untreated soils the rate of absorption of the water during the first minute was very large and gradually decreased until near complete saturation, when it was very slow. In the case of the untreated soil nearly half of its water capacity, measured from air dryness, was satisfied the first minute of contact. The soil column was about two inches high, and no doubt the lower stratum of one-half to one inch in thickness was practically saturated the first minute. While the water is in contact with

[1] Absorbed 0.2 per cent. over night.

the surface of a soil (the lower surface in the apparatus) the films of water around the soil particles grow thicker and thicker, filling more and more nearly the capillary spaces. This gradually decreases the surface-tension and therefore the rate of absorption.

The rate of movement of the zone of capillary moisture is very much more rapid than the zone of saturation. This is due (1) to the decrease in surface-tension above mentioned, (2) to the resistance with which the water meets in passing through the saturated zone, (3) that the saturated zone holds several times as much moisture as the capillary zone, requiring a correspondingly longer time to saturate it. The resistance due to the passage of water through a saturated stratum must be considerable when it is remembered that the percolation per square inch, under a pressure of one inch on this soil, is one and four-tenths cc. per hour, while the rate of absorption was thirteen cc. the first minute. It will be noticed that the decrease in absorption the first minute in the cases when the salts were present is not proportional to that of the entire time required, for saturation, as compared against these rates in the untreated soil. This is doubtless due to the fact that the salts had not fully dissolved during the first minute of contact. Yet this change is soon noticeable as the time of contact increases, showing that the effect of the salts is extremely rapid. The whole time required for the saturation of the samples is the better criterion by which to judge the effects of the salts upon the soil, which are given below:

RATE OF COMPLETE SATURATION.

Sample.	Time.
Soil	35 min.
" + 0.5 per cent. K_2O as K_2SO_4	60 "
" + 0.5 " " K_2O as KCl	180 "
" + 0.5 " " K_2O as KNO_3	180 "
" + 0.5 " " K_2O as K_3PO_4	130 "
" + 0.5 " " K_2O as K_2CO_3	35 "
" + 0.5 " " K_2O as $KHCO_3$	40 "
" + 0.5 " " K_2O as KOH	75 "
" + 0.75 " " CaO	20 "
" + 0.75 " " CaO as $CaSO_4$	30 "
" + 0.75 " " CaO as $Ca(NO_3)_2$	30 "
" + 0.75 " " CaO as $CaCl_2$	25 "

Sample.	Time.
Soil + 0.75 per cent. CaO as $CaH_4(PO_4)_2$	75 min.
" + $CaHPO_4$ (0.75 per cent. CaO)	70 "
" + $CaCO_3$ (0.75 per cent. CaO)	50 "
" + 0.5 per cent. MgO as $MgSO_4$	90 "
" + 0.5 " " $Mg(NO_3)_2$	60 "
" + 0.5 " " $MgCl_2$	60 "
" + MgO	35 "
" + 0.5 per cent. MgO as $MgCO_3$	35 "
" + 0.5 " " Na_2O as $NaHCO_3$	36 hours
" + 0.5 " " Na_2O as NaCl	24 "
" + 0.5 " " Na_2O as Na_2SO_4	80 min.
" + 0.1 " " Na_2O as $NaHCO_3$	170 "
" + 0.1 " " Na_2O as NaCl	5 hours
" + 0.1 " " Na_2O as Na_2CO_3	105 min.
" + 0.1 " " N as $(NH_4)_2SO_4$	90 "
" + 0.1 " " N as NH_4Cl	95 "
" + 0.1 " " N as NH_4NO_3	120 "
" + 0.1 " " N as $NaNO_3$	24 hours
" + 0.001 " " N as $NaNO_3$	45 min.
" + 1 molecule CaO + 1 molecule $NaNO_3$	5 hours
" + 3 " CaO + 1 " $NaNO_3$	75 min.
" + 9 " CaO + 1 " $NaNO_3$	25 "
" + 1 " Na_2SO_4 + 1 " $CaSO_4$	60 "

It will be observed that almost every salt added to the soil has had some effect in changing the rate of absorption of water. The most of them have decreased it; in some cases enormously. The lime salts (save the phosphates and carbonate) alone increase it, and that to too a very small extent. The alkaline salts of potassium, ammonium, and sodium have affected it most, in the order named. It is rather singular that the carbonates of potassium should have no effect, and that the carbonates of soda should have such a marked effect. While the absorption of water by the soil during short heavy showers is an important factor in the water supply, the quantities of the fertilizer ingredients added in practice are not enough to affect appreciably this factor, except sodium nitrate, when added to the amount of 0.001 per cent. of nitrogen has reduced the rate of saturation about thirty per cent. It is further to be noticed that the addition of those salts which increase the rate of absorption, together with those which decrease it, have a neutralizing effect upon each other in the soil. Whitney has determined the surface-tension of various salt solutions and finds that certain salts

increase and others decrease the surface-tension of water. He attributes largely to this variation in surface-tension, the beneficial effects of fertilizers in modifying the soil's power to maintain a supply of moisture.[1] These variations in surface-tension, it seems to me, are too small to affect very appreciably the soil's supply of moisture. Then he finds that potassium chloride, ammonium sulphate, sodium nitrate, and sodium sulphate increase the surface-tension of water, and that potassium nitrate, ammonium nitrate, and potassium sulphate slightly decrease it. The former then should increase the rate of absorption of water by the soil, when present, and the latter should slightly decrease it. But the results given above show that all of these salts have decreased the rate of absorption, the size and arrangement of the soil particles remaining unchanged. It is clear then that the variations in rate of absorption due to the presence of certain salts, cannot be due to an alteration in the surface-tension. They are more likely due to the breaking-down of the aggregates of the soil into smaller ones, which would increase the ratio of the surface of the spaces to their volume, or to the rearrangement of the soil particles in such a way as to effect the same thing. If this be the cause, then these same salts ought also to decrease the rate of percolation and rate of evaporation, and increase the total capillary lift of a soil when present. Wollny has discussed the arrangement of the soil particles after the following manner: "If we consider a soil divided up into its individual particles, each particle sensibly spherical and of the same size, there are three simple arrangements of the particles, each giving a different amount of vacant space. First, when each sphere rests upon two spheres in the space between them, as in Fig. 3-*A*, giving a spherical-sided tetrahedron between them, having a cross-section *A'*; second, when each sphere rests upon a single sphere over its center, as in *B*, leaving a spherical-sided cubic space between, having a cross-section *B'*; and third, an arrangement the same as the first, except having every second particle in the alternate rows omitted, as in *C*, leav-

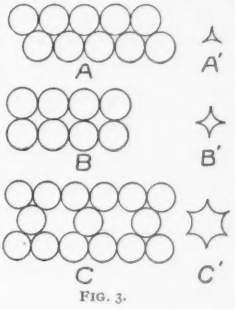


FIG. 3.

[1] Wiley's Agricultural Analysis, pp. 136-137.

ing a space with cross-section *C'*. I would call attention to the fact[1] that aggregate particles of the soil as well as simple particles, are susceptible of these three arrangements, and they are more likely to be somewhat spherical than the individual grains. The total vacant space in the first arrangement would be 30.19 per cent. of the apparent volume of the soil, in the second arrangement 47.64 per cent., and in the third 48.7 per cent. In a rearrangement of the soil particles passing from the first to the second, or to the third, there would be quite a difference in the water capacity of the soil in each. Arrangement *C* has large and small spaces. The canals in the first arrangement are zigzag, in the other two they are straight, but with undulating sides. These facts alone would modify the rate of all kinds of capillary movements of water in the soil. If arrangements *A* and *B* be in combination, then the spaces will be over each other, as in arrangements *B* and *C*, giving a total space of 38.10 per cent. of the apparent volume of soil. In these three differently shaped canals there will be a difference in the ratio of volume of the spaces to the surface area bounding the spaces in each arrangement, and therefore different capillary values for water capacity, height of lift and capillary movements in each. While it is a fact that the soil particles are not spherical, but are more or less angular, the difference in the volume of space in these arrangements would be much greater than if the particles were spherical, and, therefore, the change in capillary values would be all the greater in passing from one form of arrangement to another. In arrangement *A* the water capacity and capillary movements would be least and the capillary lift greatest, for a given size soil particle. This change in arrangement can be brought about in nature and practice mainly by mechanical agencies, and is by no means under perfect control. Cultivation and heavy freezes tend to move the soil particles apart and to place them in the more open arrangement, while heavy rains and stirring or tramping when wet tend to break up the soil aggregates into finer ones and to place them in the compact form of arrangement. In a soil, however, the particles are not round, which would increase the variation in passing from one form of arrangement to another; and

1 Expteriment Station Record, 6, No. 9, pp. 764-5.

the particles are of variable sizes, and the smaller would tend to fill in the spaces between the larger. The two effects would tend to counteract each other, and to what extent would depend upon the ratio of the number of small to large particles. But in either of these three theoretical forms of arrangement, or in any other form of arrangement conceivable, the size of the soil particles, whether simple or aggregate, would determine the ratio of volume of spaces to surface area bounding them, and in a great measure all of the capillary values of the soil. Therefore, any agent which will change the size of the soil aggregates—which will build up larger ones, or break down those existing into smaller ones—will change profoundly that soil's power to hold and maintain a supply of moisture. While it is possible to control to a useful extent the texture of the upper layer of soil by judicious cultivation, so as to keep the crop mulched with a loose layer of earth, I think the results which are to follow will show that the size of the soil aggregates in the root stratum and sub-soil in the case of fine-grained soils, is also subject to control to a useful extent, and therefore the soil's power of maintaining a supply of moisture.

WATER-HOLDING CAPACITY.

The maximum water-holding capacity of any soil depends upon the total amount of space, and the size and shape of the individual spaces in the soil, and therefore upon the size and arrangement of the soil particles. In each of the three forms of arrangement of the soil particle of uniform size, there is a size of space which will just hold all its water and which represents the largest possible "maximum water-holding capacity" of that soil. If the size of the soil particle be increased or the arrangement changed so as to give larger spaces, these spaces will cease to be capillary and the water-holding power will be decreased, and if the spaces should be made smaller from any cause the water capacity of the soil would also be decreased. But in a natural soil the particles vary enormously in size. The spaces also vary in size, but very much less than the soil particles, owing to the tendency of the smaller particles to fill in the spaces between the larger ones. Yet in a natural soil, containing canals of various sizes, a certain porosity represents the

largest water capacity of that soil, when, if its grains be pulled further apart, some of the spaces will cease to hold water, and if pulled closer together the total space is made less, and in each case the water capacity is lessened. This is true not only for the maximum water capacity, but also for the water capacity at any point along the soil column in contact with water below—from the stratum below where all the capillary spaces are filled with water, to the top of the column where the water capacity is minimum, where only the finest capillary canals can sustain that height of column of water. Since the soil canals are of varying sizes, and each will sustain a different height of column, it follows that there will be a gradual decrease in the water-holding power from the bottom where it is maximum, to the top where it is minimum. Whether or not this decrease is regular will depend, in a soil chemically homogeneous, upon (1) whether or not the soil column is uniformly compact, (2) whether the arrangement of the soil grains is the same at all points along the soil column, and (3) whether or not the decrease in the size of the capillary canals is regular. These conditions we should not expect to realize in nature, and should therefore expect to find an irregular decrease in water capacity upon ascending such a soil column. The larger the number of small soil particles which can fill in the spaces between the larger ones, the less the variation in the size of the capillary canals, and, therefore, the less the difference between the maximum and minimum water capacities of the soil. Thus any agent which would decrease the size of the soil aggregates would tend to increase the minimum water capacity of the soil, which would be an important factor in plant growth during a dry season. It is to be regretted that the many other duties required of me have prevented me from making a full study of the effects of various salts upon the minimum water capacity of soils, which I hope to be able to do some time in the near future. The maximum water capacity in the soil alone and in the presence of the various salts experimented with was determined, but there was so little difference between that of the soil alone (which was 54.4 per cent.) and that of the samples to which the various salts were added, and the variations were so irregular that it is deemed not worth while to give their results here. None of the salts increased the

water capacity, and none decreased it more than six per cent. While the water capacity of the soil is an important factor in plant growth, since it represents the soil's supply of moisture, yet the variations due to the presence of the salts are too small to be of any practical value.

PERCOLATION OF WATER THROUGH SOILS.

During the absorption of rain by a soil the capillary action and gravity act together to move the water downward until the soil spaces are filled, when the surface-tension is zero and gravity acts alone to move the water downward. The water from the surface and from the spaces in the soil, which are too large to hold their water, thus tends to percolate through the soil. This movement of the water by gravity is resisted by the friction on the sides of the capillary canals of the soil, and whether due to the friction between water and water, or between water and the soil grain, or to both, the amount of resistance is proportional to the surface area bounding the spaces. It is clear then that the arrangement of the soil grains, whether simple or aggregate, according to one or more of the three possible ways, and also the size of the soil grains in any form of arrangement whatever, will affect this ratio of volume to area of bounding surface of the capillary canals. The size of the soil particles remaining the same, the arrangement in Fig. 3, *A*, would give the lowest rate of percolation and *C* the greatest. In any arrangement, the smaller the size of the soil particles or aggregate, the less the rate of percolation, and vice versa. A study was made of the percolation through the soil alone and in the presence of a few salts, as follows: Fifty grams of soil were placed in the soil tube (of one and one-half inches in diameter) saturated with water, and a head of one inch of water added on top of the soil, so gently that the water was not muddied, and the time required for five cc. to pass through was noted. The next day one inch head of water was added again and the rate of percolation noted, and so on until the rate became nearly constant, giving the results tabulated below:

PERCOLATION PER HOUR.

No. of applications.	Days. 1st. cc.	2d.	3rd.	4th.	5th.	6th.	7th.	8th.	9th.	10th.
Soil.....	12.8	12.8	11.5	9.6	9.6	..	..	..	..	..
" + 0.5 per cent. KCl....	0.6	1.2	1.0	1.0	0.8	0.4	..	..	..	..
" + 0.5 " " KNO_3..	0.45	1.1	1.2	0.45	0.4	0.1	..	..	..	..
" + 0.75 " " CaO ...	28.0	28.5	30.0	31.2	31.0	26.5	22.8	20.2	21.0	20.8
" + 0.1 " " Na_2CO_3.	4.0	3.6	3.4	4.4	3.6	2.6	2.0	2.2	1.6	..

In the case of soil alone, it will be observed that the percolation gradually decreased until it reached its limit at nine and six-tenth cc. per hour. The motion of the water doubtless moved the finer particles into the larger spaces and filled them in, thus simulating a finer grained soil. It may be that the water broke up some of the aggregates into finer particles in addition. This gradual reduction of the percolation seems to be an office of the soil in preventing the waste of this most essential element of plant growth, and it seems to be a part of a general law of nature, *that those things which are most essential to the growth of plants, as potash, lime, phosphoric acid, ammonia, and also water, the soil tends to conserve.* By comparing the percolation through the soil alone with that of the soil when one-half per cent. of potassium chloride and potassium nitrate, and 0.75 per cent. lime were present, it will be seen that the rate of percolation was in the first two instances reduced at first to one-twenty-fifth and one-thirtieth, finally to one-twenty-fifth and one-ninety-sixth, respectively, of that through the soil alone; and in the case when lime was present, the rate was more than doubled. In the case of the potassium salts the percolation slightly increased for a time, and then decreased until it was practically nil, when the observations ceased. Indeed, it took about a week for one inch head of water to pass through the soil. The percolation in the case of the lime also increased for a time, and then decreased, becoming constant at about 20.4 cc. per hour. In the case where the potassium salts were present the soil had the appearance of being puddled, which it doubtless was, while the soil containing the lime looked granular. This fact and the preceding ones, tend to show that these changes in the percolation power of the soil, is due to a change in the size of the soil particles, and would therefore persist after the salts were removed,—how long, would depend, of course, upon the subsequent treat-

ment which the soil received. Since the surface tension during percolation is zero, the above changes in the rate of percolation cannot be due to any change in surface-tension by the salts.

Percolation after Long Standing in Contact with the Added Salts.—When the rate of percolation was determined, the water had usually been in contact with the soil for about an hour, which was sufficient time, it was believed, for most of the compounds added, to go completely into solution. However, it was thought possible that a longer time of contact might bring about a more marked change. So after the rate of percolation was determined the first time, the excess of water was removed from above the soil, that as little as possible of the salts might be washed out, and the soil allowed to stand for eighteen days, and the rate of percolation determined again each sixth day. These determinations were made with samples of soils, to each of which was added potassium carbonate, potassium chloride, potassium phosphate, calcium oxide, and calcium sulphate. The variations due to the long standing in contact with the salts were so small, the greatest being less than three per cent., that the results need not be given here. We would conclude, therefore, that the change in rate of percolation in the soil due to the presence of certain salts is effected in less than an hour's contact with the water. The decrease in the rate of percolation previously noted being probably due to the continued motion of the water through the soil, filling the larger spaces with fine grains.

RATE OF PERCOLATION PER HOUR THROUGH THE SOIL ALONE AND IN THE PRESENCE OF VARIOUS SALTS.

Sample.	No. cc. per hour.
Soil	10.2
" + 0.5 per cent. K_2O as K_2SO_4	3.6
" + 0.5 " " K_2O as KCl	1.6
" + 0.5 " " K_2O as KNO_3	1.8
" + 0.5 " " K_2O as K_3PO_4	3.1
" + 0.5 " " K_2O as K_2CO_3	8.9
" + 0.5 " " K_2O as $KHCO_3$	6.0
" + 0.5 " " K_2O as KOH	4.6
" + 0.75 " " CaO as $Ca(OH)_2$	23.0
" + 0.75 " " CaO as $CaSO_4$	12.8
" + 0.75 " " CaO as $Ca(NO_3)_2$	14.1
" + 0.75 " " CaO as $CaCl_2$	18.0
" + 0.75 " " CaO as $CaH_4(PO_4)_2$	9.8

Sample.	No. cc. per hour.
Soil + 0.75 per cent. CaO as $CaHPO_4$	9.4
" + 0.75 " " CaO as $CaCO_3$	8.0
" + 0.5 " " MgO as $MgSO_4$	8.6
" + 0.5 " " MgO as $Mg(NO_3)_2$	16.6
" + 0.5 " " MgO as $MgCl_2$	8.0
" + 0.5 " " MgO as MgO	9.0
" + 0.5 " " MgO as $MgCO_3$	9.0
" + 0.5 " " Na_2O as Na_2SO_4	4.1
" + 0.1 " " Na_2O as $NaHCO_3$	3.2
" + 0.1 " " Na_2O as Na_2CO_3	2.6
" + 0.1 " " Na_2O as NaCl	1.2
" + 0.1 " " N as $(NH_4)_2SO$	3.4
" + 0.1 " " N as NH_4Cl	2.8
" + 0.3 " " N as NH_4NO_3	2.4
" + 0.1 " " N as $NaNO_3$	0.5
" + CaO + $NaNO_3$ for 1 per cent. N	1.2
" + 3 molecules CaO + 1 molecule $NaNO_3$	5.1
" + 9 " CaO + 1 " $NaNO_3$	13.6
" + 0.1 NaO as NaCl + 0.1 per cent. $NaHCO_3$	1.2
" + Na_2CO_3 + $CaSO_4$	6.8
" + 1 molecule Na_2CO_3 + 2 molecules $CaSO_4$	9.4
" frozen	22.0
" " + 0.5 per cent. Na_2CO_3	0.2

By comparing the rate of percolation through the soil to which the various salts were added, against that through the soil alone, it will be seen that all the potassium salts used have reduced the rate of percolation, the nitrate and chloride having the greatest effects; that the nitrate, chloride, sulphate, and calcium hydroxide have increased the rate of percolation, the other lime salts having little effect; that the magnesium salts have little effect, except the nitrate which has increased the percolation; that the ammonium salts used have decreased the rate of percolation much more than the potassium salts; that the sodium carbonate and chloride, and especially the nitrate, have a remarkable effect in reducing the rate of percolation. One-tenth per cent. of soda as sodium chloride has reduced the rate of percolation to one-tenth, and one-tenth per cent. of nitrogen as sodium nitrate has reduced it to one-twentieth of the rate through soil alone.

These variations are enormous, and since the greatest effects of the salts upon the percolation are not developed during the first determination, but increase as the water

continues to pass through, it is believed that these results would show that the quantities of these salts which it is practical to add to the soil would be sufficient to make a great difference in the escape of the water of the soil by percolation, and therefore in the amount of water which a soil so treated can maintain for the growth of a crop.

The soil in which there was a great reduction in the rate of percolation, due to the presence of certain salts, in each case had the appearance of being puddled, which it undoubtedly was. Slaked lime had the greatest effect in increasing the rate of percolation, which agrees with the common experience of the farmer that lime makes the soil more open and porous. It will be observed that molecular quantities of lime added to the soil to which sodium nitrate (one-tenth per cent. nitrogen) had been added, did not restore its permeability, nor did three times the molecular quantity do so. Nine times the quantity increased the permeability to about one-third more than that of the soil alone. We therefore conclude that sodium nitrate is about seven times more effective in decreasing the rate of percolation than lime is in increasing it.

It was thought desirable to know the quantitative effect of a freeze upon the rate of percolation of a soil. After determining the rate of percolation in a sample it was allowed to freeze in the soil tube, and after thawing, the vacant space all around between the soil and the soil tube was filled in with melted paraffin. The rate of percolation was then determined and was found to be a little more than double that of the soil below freezing. After this experiment enough sodium carbonate was added to the water remaining on top of the soil to give one-half per cent. sodium oxide, and the next day the rate of percolation was determined and was found to be reduced to the extremely low figure of two-tenth cc. per hour. This was a crucial test of the puddling power of the neutral sodium carbonate. It was purposed to treat small plats of a homogeneous soil with these various salts, and after several months to cut out an oblong square from the subsoil of each and determine the rate of percolation in situ by Whitney's method,[1] but circumstances prevented.

[1] Wiley's Agricultural Analysis, I, 164.

APPLICATION OF RESULTS TO ALKALI SOILS.

As was to be expected from Hilgard's researches upon alkali soils, the neutral sodium carbonate is found to have a much greater effect in puddling the soil and therefore in reducing the rate of percolation, than the sodium sulphate. The sodium bicarbonate has a less effect than the neutral carbonate. The addition of a molecular quantity of gypsum to the soil containing the sodium carbonate, as was expected, had increased the rate of percolation of the soil containing the latter, but not to that of the untreated soil, for the sodium sulphate which is thus formed, itself reduces considerably the rate of percolation through the soil, while the calcium carbonate formed has very little effect in increasing it. When twice the molecular quantity of gypsum is added, the excess from the reaction with the sodium carbonate about neutralizes the puddling effect of the sodium sulphate, and brings the rate of percolation back to nearly that of the untreated soil. Hilgard has noticed that certain quantities of alkali present in a soil is highly advantageous to a crop in the semi-arid region by increasing the moisture in the soil. It seems to be one of the compensating forces of nature that the presence of the alkali in the soil, which is the result of a scarcity of rainfall, is the means of conserving for plant growth the little water which does fall.

I would suggest the following as a quick method of determining the quantity of ameliorant needed to relieve the excessive puddled condition of alkali salts: Establish as near as possible a standard for those factors which govern the soil's supply of moisture by determining the rate of capillary rise, rate of saturation, rate of percolation, rate of evaporation, etc., in those semi-alkali soils which are yielding the best crops, then by adding constantly increasing quantities of the gypsum to samples of soil from the alkali spots to be treated, the quantity required to bring the soil back to the standard may be determined to a close approximation. In this way the needs of the soil would be indicated without waiting for a year of experimentation with a crop.

RATE OF EVAPORATION AND RATE AND HEIGHT OF CAPILLARY LIFT.

The rate of evaporation from the soil depends upon the sur-

face area exposed and the motion, temperature, and humidity of the air, which would be approximately the same for a given surface of any soil, exposed at the same time and under the same conditions; and, also, upon the power of the soil to supply water to the surface by capillary action. In a column of soil full of water exposed to evaporation, the cavities in the soil which are full of water will give up their contents to both the large and small capillary canals which will deliver the water to the surface to meet the evaporation and plant use. As the lowering of the level of water thus proceeds, the largest capillary canals will cease one by one to deliver their water, and the rate of delivery, and, therefore, of evaporation, will gradually decrease, and the level will lower until the limit of the lift of the smallest capillary canal is reached, when the evaporation will be almost nil. In the case of a long column of air-dried soil placed in contact with water below, the rate of rise is also very rapid at first, for at first all of the capillary canals are lifting the water, the large ones very rapidly, and some of the water from the larger ones is moving laterally into the smaller canals. The larger canals, one by one, reach their limit of lift and cease to carry water, leaving the smaller and smaller ones to carry it as the capillary rise proceeds. Now the rate of rise in the smaller canals is very much slower, and some of the water from them is drawn out laterally to increase the moisture of the grains whose canals are too large to carry the water at that height. Both of these act together to reduce gradually the rate of rise of the visible capillary moisture, as the height of column increases. Both the height and rate of capillary lift will depend upon the ratio of the total amount of surface-tension acting upward (1) to the weight of the water for the height of lift; (2) to the surface area of the walls of the capillary canals, for the rate of rise. Any agent which will vary the surface-tension of the soil water, or rearrange the soil grains so as to change the shape of the capillary spaces, or change the size of the soil aggregates, will alter this ratio, and therefore the height of capillary lift, rate of capillary rise, and rate of evaporation of the soil, as well as the rate of saturation. The rate of evaporation was determined by placing twenty-five grams of the sample of soil to which the various salts had been added, in flat dishes of equal size, to each

of which enough water was added to saturate the soil, when they were weighed, set aside for evaporation to take place, and weighed each day. The dishes were shallow and the soil was about three-fourths of an inch deep. It is to be regretted that vessels of the same dimensions as the soil tubes were not at hand, for the capillary lift in these experiments is so small, and, therefore the difference in rate of ascent, that the differences in evaporation are not what they would be in deep vessels. The capillary tests were made in the usual way by filling long tubes with soil and placing them in separate vessels of water kept to a pretty constant head. The tubes used were sixty inches long and one-fourth inch bore. They were filled by attaching a small filter tube to the end of the long tube into which the soil was added, little by little, and was jolted down into the long tube by letting fall from a constant height an equal number of times. Since the soil fell into the tube at the same time it was being jolted down, the tendency to stratify, pointed out by Hilgard, was minimized. An examination showed very little stratification. These tubes were filled as nearly in the same way, and jolted as nearly the same as could be done. In order to test the uniformity of the tamping, the one containing soil alone was filled first, and after all the others were filled a duplicate was filled with soil alone. The ascent of the two was within one inch of each other. It was not possible to keep a detailed record of the rise of each; the heights were taken after twelve and sixty days. It is to be regretted that the unexpected termination of the Louisiana Sugar School, and the unwillingness of the Experiment Station connected therewith to take up the work, terminated my observations before many of the soil columns had ceased to lift their water. However, from the two records, the comparative rate of rise may be had, and in some cases the height of lift, and is given below in inches after twelve and sixty days. The percentage of evaporation is calculated upon the total amount of water which was added, in order to saturate the air-dried soil. It is thought not worth while to give the rate of evaporation from day to day, as the ones for the day selected the third day showed the maximum differences in evaporation.

EVAPORATION AND CAPILLARY RISE.

Sample.	Evaporation. Per cent.	Capillary rise. 12 days. Inches.	Capillary rise. 60 days. Inches.
Soil alone	55.4	25	45
" + 0.5 per cent. K_2O as K_2SO_4	50.14	17.5	37
" + 0.5 " " K_2O as KCl	50.21	15.5	32
" + 0.5 " " K_2O as KNO_3	48.8	13.0	26.5
" + 0.5 " " K_2O as K_3PO_4	53.02	17.8	34
" + 0.5 " " K_2O as K_2CO_3	55.33	18.5	37
" + 0.5 " " K_2O as $KHCO_3$	56.16	17.9	37
" + 0.5 " " K_2O as KOH	50.72	22	38
" + 0.75 " " CaO as $Ca(OH)_2$	50.75	26	...
" + 0.75 " " CaO as $CaSO_4$	51.72	31	53.5
" + 0.75 " " CaO as $Ca(NO_3)_2$	57.81	21	33
" + 0.75 " " CaO as $CaCl_2$	50.82	24	38
" + 0.75 " " CaO as $CaH_4(PO_4)_2$	59.93	22	42.5
" + 0.75 " " CaO as $CaHPO_4$	52.04	24.5	46.5
" + 0.75 " " CaO as $CaCO_3$	50.33	28.2	57.5
" + 0.5 " " MgO as $MgSO_4$	49.51	21.3	36
" + 0.5 " " MgO as $Mg(NO_3)_2$	50.40	21	39
" + 0.5 " " MgO as $MgCl_2$	54.82	23	54
" + 0.5 " " MgO as MgO	63.75	29	47.5
" + 0.5 " " MgO as $MgCO_3$	64.42	31	50

It will be observed that of the salts experimented with, potassium nitrate and potassium chloride have exerted the greatest influence in retarding both the rate of evaporation and the rate of capillary rise in the soil, and that magnesium oxide and magnesium carbonate have increased these two factors most. As a rule, those compounds which affect evaporation most affect the rate of capillary rise and in the same direction. The calcium superphosphates and the potassium carbonates are exceptions to this general rule. The hygroscopic nature of some salts would have some effect in retaining moisture *per se*, and independent of any modification of the arrangement or of the size of the soil particles, or of the surface-tension of the soil water. However, a glance at the rates of evaporation as given above, shows no changes which are proportional to the hygroscopicity of the salts used. In the column of untreated soil the capillary rise reached its limit at fifty inches in 110 days, column of soil plus the gypsum fifty-one inches in sixty-eight days, the soil plus calcium carbonate fifty inches in seventy-two days, soil plus calcium superphosphate fifty-one inches in 105 days,

soil plus magnesium oxide forty-seven inches in eighty days, and soil plus magnesium carbonate forty-seven inches in seventy days. The soil column containing potassium sulphate was still rising when it reached the end of the tube at sixty inches in 140 days. This is an increase of five inches in height over that in the untreated soil. It is most probable that those salts such as potassium chloride and potassium nitrate, which reduced the rate of rise more than potassium sulphate, would also have increased the height of lift more than did the potassium sulphate. It seems to be a general rule then that those salts which when added to a soil reduce the rate of rise of capillary moisture, increase the height of lift; and conversely that those salts which increase the rate of rise, decrease the height of lift. These variations in rate and height of capillary lift, and in rate of evaporation, do not correspond to the changes in the surface-tension of water caused by these salts, as was found to be true in the study of the rate of saturation and percolation. It is to be regretted that the rate of evaporation and the rate and height of capillary rise was not determined also in the soil to which the sodium and ammonium compounds were added, that the results might appear in this statement, but it was impossible to do so.

On account of the great length of time for the capillary moisture to reach its limit of rise, it is most desirable that an empirical formula be developed for calculating the height of lift from some easily determined factors. Since the maximum water capacity is the same as the quantity of water held in a soil column just above the level of the water which is in contact with it, and the minimum water capacity is about the same as the amount of water at the limit of the capillary rise, and since the rate of capillary rise, as determined in the soil apparatus described, gives the rate of rise for the height of column used, it seems that these three factors which are so quickly determined, together with the total height of lift, would furnish the necessary data for such a formula. It is my purpose to attempt to work out such a formula sometime in the near future.

GENERAL DISCUSSION OF RESULTS.

It will be noticed, in general, that the four principal factors which govern the soil's supply of moisture—the rate of satura-

tion, of percolation, of evaporation, and of capillary rise—when changed by the addition of a salt to the soil, all vary in the same direction, and oppositely, to the height of lift. This would indicate that these changes are due to a common cause. And since the soil assumed a puddled appearance in the presence of each of those salts which reduced these factors, and since sodium carbonate (which is one of that number) is known to puddle the soils, there can be little doubt that the decrease in the rates of percolation, etc., is due to a breaking up of the soil aggregates into smaller ones, and also that the increase in these factors is due to a building up of the soil aggregates into larger ones. And yet it is the common experience of chemists that the neutral salts cause the formation of aggregates and precipitate fine clay when held suspended in water, and that ammonia, caustic alkalies, and their carbonates and phosphates hinder such flocculation. While these facts apparently contradict my results, except[1] in the case of sodium carbonate, it must be remembered that the result in the two instances are obtained under quite different circumstances. In the one case the soil aggregates have been broken up completely; only the finest particles, almost all of which are plastic colloidal clay, are present, and they, in suspension, where they are free to move together and form aggregates large enough to settle to the bottom when salt is added to the water. Indeed all of our knowledge of the building up and breaking down of soil aggregates was obtained by the study of the behavior of soils suspended in water. In the other case, the soil mass is composed mainly of aggregates which are themselves composed of many constituents besides clay, and the fine particles are not so free to move in the water of the soil as when in suspension.

APPLICATION OF RESULTS TO AGRICULTURE.

It will be noticed that of the salts experimented with, those which most frequently occur in commercial fertilizers as potassium sulphate, calcium superphosphate, ammonium sulphate, etc., except sodium nitrate, would have very little effect when added in the quantities usual in practice upon the soil's supply of moisture, so their beneficial effects upon crops must be attrib-

[1] Wollny: Experiment Station Record, 6, No. 9, p. 766.

uted mainly to the plant-food added. But the carbonates, chloride, and nitrate of soda, have a much greater effect. While the addition of these salts would decrease greatly the rate of absorption of water, and would be of consequence in a puddled soil during a short shower, yet such a soil would become saturated during a long rainy spell—certainly during the spring rains. Then the supply of water absorbed would be more perfectly conserved in such a soil from three causes acting together, (1) the water would percolate more slowly out of the drains or out of capillary reach in the puddled soil; (2) it would rise more slowly to the surface to supply evaporation or plant growth, the delivery of the water would therefore be more constant and of longer duration; and (3) the capillary reach would be increased probably several inches, giving this much greater reservoir of ground water to draw from. Add to this the fact that the full effect of the salt added is not developed immediately (and therefore is not shown in the above analyses), and the increased puddling effect of cultivation when any of these salts are present, and it will be seen that the addition of these salts in the quantities within the reach of the farmer will be sufficient to increase considerably the soil's power to conserve its supply of moisture. Since different kinds of crops require for their highest development, according to their nature and period of growth, quite different amounts of water, a fair degree of control of the soil's power to maintain a supply of moisture, would adapt the soil to the high development of that crop (growing in that climate), which would yield the greatest financial return to the farmer. Since the rain falls at irregular periods, and there are generally times of great need of water by every crop, the ability to increase the soil's conservation power of moisture is more important than the power to decrease it; hence we have in the carbonates, chloride, and nitrate of soda, powerful agents for regulating the soil's moisture in accordance with the need of a given crop. Since water is the most essential material for plant-growth, the farmer should fertilize with regard to the soil's need of moisture as well as regards its need of plant-food. If this were done no one can predict what the increase in yield would be. In a commercial fertilizer one material often neutralizes the moisture-maintaining effect of another. For example, in kainit

the loosening effect of the gypsum would about neutralize the puddling effect of the potassium sulphate. Again, to add sodium nitrate to a soil which is too retentive of moisture by nature, to supply a deficiency of nitrogen, would actually do harm. But in the case of a soil which does not maintain enough moisture for a given crop, if the soil needs nitrogen also, sodium nitrate would give the best returns. But if this soil needed no nitrogen the carbonates or chloride of soda would remedy the moisture deficiency. These results explain why sodium nitrate gave no increased yield, even with sugar-cane, which requires an abundance of moisture upon the wet soils of Louisiana. At the Louisinna Experiment Station sodium nitrates in most cases actually decreased the yield. As was to be expected in the case of these soils, the heavy application of lime gave good returns. But lime is a very much less powerful loosening agent (about one-seventh) than sodium nitrate is a puddling agent. Lime and magnesia are the most powerful compounds found so far for decreasing the water-conserving power of soils. Doubtless a mixture of the two, easily obtained by burning a magnesium limestone, would be a still more effective agent.

Since it has been shown that in one and the same sample of soil the addition of one-tenth per cent. of nitrogen as sodium nitrate decreases the rate of percolation through the soil to more than one-twentieth of that through the untreated soil, and that the addition of 0.75 per cent. of lime has increased the rate of percolation to more than double, it is clear that the chemical composition, or the kinds and amounts of the soluble bodies of the soil have an enormous effect upon the moisture-maintaining power of a soil. This is at variance with Whitney's conclusion that the fineness of the soil particle (meaning the ultimate particle) and in general the percentage of clay determine the amount of moisture that a soil will maintain.[1] If he had said, "the fineness of the soil particle and the soil *aggregates*," the statement would have been more nearly correct. For it has just been shown that in a fine-grained soil containing a large per cent. of clay, certain salts can build up the particles into aggregates or the aggregates into larger ones, thus simulating an open coarse-grained soil; and other compounds can break down the

[1] Bull. No. 21, Nevada Experiment Station.

aggregates into smaller ones or into the ultimate particles, making an extremely close and nearly impervious soil. The percentage of clay present is a very important factor in that it furnishes the materials for the formation of these aggregates, and the greater the quantity present, the greater the range of variation in texture possible, it would seem.

A NEW METHOD OF EXAMINING SOILS.

By means of the improved soil instrument previously described, and from the results obtained, we have a new method for the quick examination of soils. A method which, it is believed, will give positive information concerning the moisture needs of a soil and therefore concerning the kind of crop best adapted to it, and also the kind of fertilizers or of chemical compounds to which the soil will respond most favorably in accordance with the moisture needs of a particular crop to be grown on that soil.

The results thus obtained, construed with the chemical and physical analysis of the soil, it is believed, will give enough information concerning the soil's needs, so that it will not be necessary to wait a year for field experimentation to advise the farmer as to the needs of his soil.

A NEW LINE OF FIELD EXPERIMENTATION SUGGESTED.

The results embodied in this paper show that fertilizers or chemical compounds should be added to the soil with a regard to the soil's moisture needs as well as its plant-food needs, and especially with regard to the control of the soil's moisture, so as to meet the requirements of a given crop. I would suggest this as a profitable and fruitful line of field experimentation for the Experiment Stations to take up. In the plots thus treated with regard to the moisture needs of crops, the yield per acre, quality of crop, the temperature of the soil, the percentage of moisture the soil maintains, the rate of percolation in situ by Whitney's method, and the like, may all be carefully studied. This, it is believed, would extend very greatly our knowledge of practical agriculture.

All the compounds used in these experiments were chemically pure. It is my purpose, however, to try the effects of the various commercial forms of fertilizers, and of natural products singly, and in the most general combinations, upon the soil with which

I am working. The incompleteness of this report is to be accounted for by the fact that this piece of work was done during such spare time as I could find while teaching three classes with laboratory superintendence every afternoon.

THE RAPID ESTIMATION OF URIC ACID IN URINE.[1]

By E. H. Bartley.

Received May 31, 1897.

THE estimation of uric acid presents well recognized difficulties, and the results obtained by any of the known methods are always open to criticism on the side of accuracy. While we admit this fact, it must also be admitted that the object for which the estimations of uric acid in urine are usually undertaken, does not require extreme accuracy. For diagnostic purposes, slight errors may usually be disregarded. Another factor often regarded by both the person afflicted and the physician, as of great importance, is the time and trouble and hence the expense to be incurred in making a correct diagnosis. The methods now in vogue for the estimation of uric acid are so time-consuming that only the chemist with a well-appointed laboratory can undertake them. This fact has prevented the mass of physicians from having such estimations made, and has deprived many unfortunate sick from the benefits to be derived from a scientific diagnosis of their ailments.

A very considerable number of methods have been proposed for the estimation of uric acid. One of the oldest methods depends upon the fact that the acid is almost insoluble in water acidulated with hydrochloric acid. The acid is set free by hydrochloric acid, and after forty-eight hours it is collected on a filter, dried at 100° C., and weighed. This method has been shown to be very unreliable, as a very considerable amount of uric acid may remain in solution. Fokker, Salkowski, and Hopkins precipitate the uric acid with ammonium chloride as acid ammonium urate, filter, wash, decompose with hydrochloric acid, let stand two hours, filter, wash, dry, and weigh on the filter. Or, the precipitated ammonium urate may be titrated with potassium permanganate, or with twentieth-normal acid. It has also been proposed to treat this precipitate with Fehling's or Pavey's copper solution, both of which are reduced by uric

[1] Read at the meeting of the New York Section, May 7, 1897.

acid, and thus arrive at the amount of the acid present by the amount of copper reduced. Either of these methods necessitates a rather troublesome filtration of the gelatinous ammonium urate.

Bayrac evaporates the urine to dryness, treats the residue with hydrochloric acid, washes the residue with alcohol, transfers to a special apparatus, and heats nearly to boiling with a solution of sodium hypobromite, and collects and measures the nitrogen, as in an urea determination. Haycraft precipitates the uric acid with silver nitrate in excess, in presence of ammonia, filters with the aid of a filter pump, dissolves the precipitate in nitric acid, and estimates the silver in the solution by Volhard's method, from which he calculates the uric acid.

This method has been much used, in spite of the numerous observers who have shown that the results are too high, on account of the fact that xanthin, hypoxanthin, and possibly other substances are thrown down by silver nitrate. Ludwig precipitates with an ammoniacal silver nitrate solution, in presence of an excess of magnesium mixture, filters, washes, decomposes the silver magnesium urate with sodium hydrogen sulphide, filters off the silver sulphide, evaporates the filtrate to a small bulk, acidifies with hydrochloric acid, lets the mixture stand to crystallize, filters through glass wool, washes, dissolves out any sulphur with carbon disulphide, dries at 100° C., and weighs.

This method is a modification of that used by Salkowski, but the latter[1] claims the priority for Ludwig's modification. Moreover, he states that hydrochloric acid does not precipitate all the uric acid from its solutions, and quotes the results of Maly and Hoffman,[2] who have shown the same thing. They found that silver nitrate will always precipitate some uric acid in the filtrate from the hydrochloric acid. Salkowski, in the same article, after a somewhat critical review of a number of the methods that have been proposed, declares that the methods of Haycraft, Hermann, and Czapek are all unreliable.

Salkowski claims to have been the first to propose the precipitation of uric acid by silver nitrate in an ammoniacal solution.[3]

1 *Ztschr. phys. Chem.*, **14**, 34.
2 *Pflüger's Archiv.*, **6**, 201.
3 *Virchow's Archiv.*, **52**, 61.

He then proposed to add an excess of silver nitrate, filter, acidify with nitric acid, filter, and estimate the excess of silver as chloride. Since then, he has thrown some doubt upon the constancy of composition of the silver compound with uric acid, upon which the method is based. Other authors have not all accepted this conclusion, and several have based processes upon the supposition that the composition of the double urate of silver and magnesium is a definite compound. It is admitted that the silver urate undergoes a partial decomposition during the rather tedious process of filtration and washing. Haycraft and Hermann both claim that this is not the case when the urine is treated with sodium bicarbonate and ammonia, before adding the silver solution, and hastening the filtration by means of the filter pump.

Cammerer[1] proposes a method in which he removes the phosphates with magnesia mixture, and then precipitates the uric acid with silver nitrate, filters, dries the residue, and estimates the nitrogen by the Kjeldahl method, and calculates the uric acid from the nitrogen found. This method avoids the following source of error in Ludwig's process. In decomposing the precipitated urate of silver with hot solution of alkaline hydrogen sulphate, a part of the uric acid is decomposed, as pointed out by Hopkins and E. Groves.[2] It has been proposed by several authors to estimate this acid by precipitation with a mixture of copper sulphate and sodium bisulphite, and estimation of the nitrogen in the precipitate. Arthaud and Butte have proposed a method by the use of a standard solution of cuprous thiosulphate. Martin Krüger[3] proposes a process based upon this principle, which he claims gives good results. Balke states that this process is not reliable when applied to the urine.

From this hasty and incomplete review of the methods that have been proposed for the estimation of uric acid in the urine, it will be seen that the processes are complicated as a rule, and the results are not in all cases reliable. As remarked above, none of these methods are rapid enough to be considered as clinical methods.

Czapek[4] has proposed a process intended to shorten the time

[1] *J. Chem. Soc.*, **56**, 1040.
[2] *Chem. News*, **66**, 107.
[3] *Ztschr. phys. Chem.*, **21**, 311.
[4] *Ztschr. phys. Chem.*, **12**, 502.

required. He adds to 150 cc. urine, eighteen cc. of a tenth-normal solution of silver nitrate, thirty cc. of a twenty per cent. ammonia, and fifteen cc. of magnesia mixture. The volume is now brought to 300 cc. and filtered through a large filter. Fifty cc. of this filtrate are taken for the titration, to determine the amount of silver in the solution. This is done in a flask by a solution of sodium hydrogen sulphide or potassium hydrogen sulphide. The flask is stoppered with a cork containing a small glass tube, to serve as an outlet for steam when the contents of the flask are boiled. The sodium hydrogen sulphide is added until the steam from the flask browns a strip of lead paper held before the outlet tube. The sodium hydrogen sulphide is then titrated against the silver solution in a similar manner. The amount of silver found in the filtrate, deducted from that added to the urine, gives the quantity precipitated with the uric acid. The results obtained by Czapek were good when pure uric acid was operated upon, but far from satisfactory when applied to the urine. The sources of error in this process are:

1. Too large a factor in uric acid for one cc. of the silver solution.

2. The precipitation of the xanthin bases by silver nitrate, and their calculation as uric acid, as in the Haycraft process.

3. The reduction of a part of the silver nitrate to metallic silver, while boiling the filtrate during the titration. This loss of silver is reckoned as having been precipitated with the uric acid.

4. In making up the solution to 300 cc., after precipitating the uric acid and magnesium ammonium phosphate, no account is made of the volume of this precipitate. In one trial he found the precipitate to measure seven and a half cc.

Errors 2 and 3 will be very considerable in fever urines, and in all concentrated urines, as his results show.

The author shows that the error, as compared with Ludwig's process, is from 0.002 to 0.004 gram in 100 cc. of normal urines, while in fever urines it reached in one case as much as 0.023 gram.

I have devised a process of direct titration, which I believe corrects most of these errors. The method is based upon the

complete precipitation of uric acid from the urine by silver nitrate, in the presence of an excess of magnesia mixture and ammonia, and the detection of the end reaction by potassium, sodium, or ammonium hydrogen sulphide. The titration is performed in a hot solution, to prevent the precipitation of the xanthin bases by silver nitrate.

The process is conducted as follows: To fifty cc., or 100 cc., of the clear urine, add five cc. of the magnesia mixture and about ten cc. of ammonium hydroxide (sp. gr. 0.960), or enough to give a decided excess. Warm the solution on a water-bath, and add from a burette a fiftieth-normal solution of silver nitrate. From time to time a drop is removed from the solution, by means of a dropper pipette, with a bit of absorbent cotton wound tightly over the end, so as to make an efficient filter, and after removing the cotton filter, bring it in contact with a drop of the weak sodium hydrogen sulphide solution on a white surface. Experiments with pure water, showed that it required one-half cc. of the silver solution in fifty cc., or one cc. in 100 cc., to give a marked reaction. This amount must therefore be deducted from the reading. The titration is continued until a dark ring or cloud is seen at the line of contact of the two drops, showing the presence of silver in the solution. Each cc. of silver solution corresponds to 0.00336 gram of uric acid, and the number of cc. used (less one-half cc. for each fifty cc. of urine) multiplied by this factor, gives the number of milligrams of uric acid in the urine taken. From this we may easily calculate the amount excreted in twenty-four hours, the only figure of clinical value.

As soon as the process is complete the precipitate rapidly settles, and it is best to draw off a drop or two from this clear supernatant liquid and test it carefully again. We may also check our work by running in another drop of the silver solution, to see if it produces a cloud, or to see if the precipitation be complete. As there is no excess of silver in the hot liquid at any time, there can be no reduction of silver.

If, after the titration is complete, the solution be cooled, it will usually be found that it will require from one to three cc. of the silver solution to again produce the end reaction, because of the

precipitation of the xanthin bases by the silver, in a cold solution.

This amount is usually greater in concentrated and fever urines than in normal urines, and it is this fact that invalidates Salkowski's older process, Haycraft's, Czapek's, and Denige's methods, in such urines, as they all depend upon the estimation of the excess of silver in the filtrate from the precipitated uric acid. I have found that the xanthin bases are but slightly, if at all, precipitated by silver nitrate from hot urine. It is shown in the following way:

Baginski, of Berlin, has shown that Hofmeister's method of precipitation with hydrochloric and phosphotungstic acids completely removes xanthin bodies from urine. This is confirmed by Alexander von Pohl, who, in a communication to the Paris Academy of Sciences, October 10th, 1892, uses this reaction for the qantitative estimation of leucomaines in urine. Baginski[1] makes use of this precipitation of these bodies for their quantitative estimation. He found normal urine to contain about 0.0027 to 0.003 gram of xanthin bodies in 100 cc. of urine.

I found, by a series of trials, that the titration of a hot urine gave the same result as the same urine after the removal of the precipitate produced by hydrochloric and phosphotungstic acids, and filtered while hot. In the cold solution a part of the uric acid is also thrown down, but this is soluble in hot water, as I have also proved, by trials with solutions of pure uric acid.

I have found the difference between the hot and cold titration, in normal urines, to be usually about one cc. in fifty cc., but in abnormal urines it has been as high as three cc. If we accept the formula of the silver xanthin precipitate, as $Ag_2O,C_5H_4N_4O_2$, the factor for the fiftieth-normal silver nitrate will be 0.0015 gram. This would give for 100 cc. $2 \times 0.0015 = 0.003$ gram for the average amount of xanthin bodies, calculated as xanthin. It will be seen that this agrees with the results found by Baginski. In febrile urines, and in concentrated urines the amount of these bodies is greater.

On one occasion, a specimen of morning urine passed by a healthy man, after an unusually hearty meal accompanied by some champagne, and followed by a night without sleep and

[1] *Ztschr. phys. Chem.*, 8, 399.

with hard work, gave a difference between the hot and cold titration of three cc. in fifty cc. of urine, instead of one cc., as on the preceding day. We have here, then, a method that gives important information outside of the quantity of uric acid. I have not had time to investigate how completely we can separate uric acid from the xanthin bases, by this process, but the results seem to point to it as a valuable clinical method, for their quantitative estimation. It has the advantage over all other methods with which I am acquainted, in that it avoids the necessity of any filtrations, and is a direct titration instead of an indirect one. It is simple, and gives good results when applied to solutions of pure uric acid. A solution of pure dry uric acid was made, with the assistance of sodium phosphate and just enough sodium hydroxide to make the solution clear, and containing one gram to the liter. Fifty cc. of this solution, containing 0.050 gram uric acid required 15 to 15.5 as the result of a number of titrations. As it took one-half cc. of the silver solution to give the reaction in fifty cc. of water, we have, after deducting this amount, 14.5 and 15 as the limits of test. This gives 0.04872 to 0.0504 as the variations in the results obtained. These results were repeated on three separate solutions. The process was then tried as follows: Fifty cc. of urine was measured out and titrated, cold, to the appearance of the end-reaction. Fifty cc. of the above solution of uric acid was then added, and the titration continued. It required sixteen cc. of the silver solution. Deducting one cc. from the result, we have fifteen cc. as the corrected reading, which agrees with the reading with the pure uric acid solution. It seems, therefore, that it is possible to estimate by this method with reasonable accuracy, uric acid in watery solutions, and to obtain good results in estimating the acid in urine to which it has been added. I regret that I have not had time to compare the result obtained by this process with those obtained with other metnods. It has become general to compare new methods with Ludwig's, which gives lower results than most others. It seems to me likely that the results obtained by such a complicated process are likely to vary. The author admits that the results are about two per cent. low, and this has been confirmed by others. The

following is the result of three estimations made by my method as compared with Ludwig's:

	Ludwig. Gram.	Direct titration. Gram.
No. 1. Uric acid in 100 cc ...	0.0822	0.08064
No. 2. " " " 100 " ...	0.0506	0.05370
No. 3. " " " 100 " ...	0.0684	0.07064

The relation of uric acid to urea is generally regarded as an important guide in the determination of a normal or abnormal excretion of uric acid, and it is believed by many to be more important than a statement of the actual amount of uric acid eliminated. This ratio is variously stated as from one to thirty-three, to one to sixty. The ratio varies with the method used for the estimation of uric acid. In the above three urines the ratio was as follows:

	Ludwig.	Direct titration.
No. 1	1 to 33.7	1 to 34.4
No. 2	1 to 37.0	1 to 34.8
No. 3	1 to 50.0	1 to 48.5

Although the number of comparative tests is too small to prove the entire reliability of the process, as compared with Ludwig's, these results indicate that it is a valuable clinical method. It is also valuable as a rapid and approximately accurate method of estimating the unoxidized xanthin bases, which have an important clinical bearing, when present in the urine in excess.

In conclusion, I would call attention to the fact, that the results by this process are more apt to be higher than the truth, than lower, on account of the difficulty of seeing the first appearance of the dark cloud, in the test. It will, therefore, be best in individual cases, for the observer to make a test of the process with a solution containing a known amount of uric acid, as a guide to the appearance of the end-reaction. With a little practice, the end-reaction can be determined with accuracy.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 22.]

THE ATOMIC MASS OF TUNGSTEN.

BY WILLETT LEPLEY HARDIN.

Received June 17, 1897.

A REVIEW of the literature on the determinations of the atomic mass of tungsten will show that a careful examination of the methods employed is of fundamental importance. Fifteen experimenters have made determinations of this constant, but with widely varying results. The method of investigation, with few exceptions, has been to reduce tungsten trioxide in a current of hydrogen at a white heat, and then to reoxidize the metal thus obtained. Deviations occur not only in the results of the different experimenters but also, with few exceptions, in the different observations of the same experimenter. Clarke[1] closes his summary of all the work on the atomic mass of tungsten with the following words: "Farther investigation is required in order to fully establish the true atomic weight of tungsten."

Deviations in the results of any atomic mass determination are due either to an inaccurate method or to experimental errors. It is not always an easy matter, however, to determine the source of error in a given series of variable results; but with several series of results from different experimenters, the question can be decided with a reasonable degree of accuracy. If, for instance, we have several series of results by the same method from different experimenters, and if the different series, with the exception of one, agree with each other, the probability is that the deviations in the one series are due to experimental errors. If, on the other hand, deviations occur in each series, and are more or less similar, the probability is that the method is inaccurate.

Almost every series of results on the atomic mass of tungsten, obtained by the reduction of the trioxide in a current of hydrogen, and by the reoxidation of the resulting metal, shows a variation between the maximum and minimum results of from one to two units, and in exceptional cases the deviation is much greater. In view of these facts, it seems desirable to make a

[1] A Recalculation of the Atomic Weights, 1897.

careful study of the method which has usually been employed in this work, rather than add to the already large number of results; for, if the method is unreliable, no experimental skill can make the results trustworthy.

The following summary will show the lack of concordance in the results of the earlier determinations:

Berzelius[1] was the first to determine the atomic mass of tungsten. By reduction of the trioxide he obtained the value 189.6 as a mean of two experiments for the atomic mass of tungsten. The difference between the two results was 3.0. These results and those that follow are calculated on the basis of O = 16.

Schneider,[2] working with material which had been carefully purified, obtained two series of results for the atomic mass of tungsten, one by the reduction of tungstic acid and the other by reoxidation of the metal.

Reduction series.		Oxidation series.
184.18		184.21
183.37		184.16
184.01		183.36
184.28		
184.45	Maximum difference	0.85
Maximum difference 1.08		

The quantity of material used in these experiments varied from two to six grams.

Marchand[3] reduced the trioxide of tungsten and reoxidized the resulting metal; the following results were obtained for the atomic mass of tungsten:

183.91	Reductions.
183.96	
184.16	Oxidations.
184.51	
Maximum difference 0.60	

Borch[4] made seven reductions of tungstic acid in a current of hydrogen, and two oxidations of the metal. The results were as follows:

[1] *Pogg. Ann.*, **8**, 1, *1826*.
[2] *J. prakt. Chem.*, **50**, 152, *1850*.
[3] *Ann. Chem. Pharm.*, **77**, 261, *1851*.
[4] *J. prakt. Chem.*, **54**, 254, *1851*.

Reductions.		Oxidations.
184.10		184.53
182.90		184.32
183.77		
184.10	Difference	0.21
183.03		
183.77		
183.91		
Maximum difference 1.20		

The quantities of material varied from two to eight grams.

By weighing the water obtained in the reduction of tungstic acid in hydrogen, Riche[1] obtained the value 174 for the atomic mass of tungsten as a mean of two experiments. The difference between the two was 1.78.

Dumas[2] reduced the trioxide of tungsten in hydrogen and obtained the following results for the atomic mass of tungsten.

184.00
183.42
184.16
183.76
183.62
184.80
184.16
184.08

Maximum difference = 1.38

The quantities of material varied from one to four and six-tenths grams.

Bernoulli[3] reduced tungstic acid at a very high temperature in a current of hydrogen. The results were as follows:

Reduction series.		Oxidation series.
186.78		186.81
185.86		187.94
186.75		186.77
186.81		186.76
186.70		— —
177.73	Maximum difference = 1.18	

Maximum difference = 9.08

The maximum difference in the two series is 10.21. He found

[1] *J. prakt. Chem.*, 69, 10, *1857*.
[2] *Ann. Chem. Pharm.*, 113, 23, *1860*.
[3] *Pogg. Ann.*, 111, 573, *1860*.

that the greenish colored oxide gave the same results as did the yellow oxide.

Persoz[1] made two reductions of the trioxide of tungsten and obtained concordant results.

183.93
183.94

Difference = 0.01

Scheibler[2], from determinations of the water in barium meta-tungstate, obtained the value 184.00 for the atomic mass of tungsten. Maximum difference = 1.03.

Zettnow[3] obtained the value 184.08 for the atomic mass of tungsten as a mean from four analyses of the tungstate of iron. From silver tungstate he obtained the value 183.80.

Roscoe[4] made three reductions and two oxidations of the same sample of material, beginning with 7.8840 grams of tungstic acid. The results were as follows:

Reductions.	Oxidations.
182.72	182.49
183.71	183.87
183.97	
Maximum difference = 1.25	Difference = 1.38

From two analyses of tungsten hexachloride, Roscoe obtained the value 184.25 for the atomic mass of tungsten.

Waddell,[5] from carefully purified tungstic acid, obtained by reduction in hydrogen the following values for the atomic mass of tungsten:

184.55
184.37
184.59
184.00
183.67

Maximum difference = 0.92

The quantities of material varied from one to four and a half grams.

1 *Ann. Chim. Phys.* [4], 1, 93, *1864.*
2 *J. prakt. Chem.*, **83**, 324, *1861.*
3 *Pogg. Ann.*, **130**, 30, *1867.*
4 *Ann. Chem. Pharm.*, **162**, 368, *1872.*
5 *Am. Chem. J.*, **8**, 280, *1886.*

The material used in the work of Pennington and Smith[1] differed from that of all the preceding experimenters, in that the last traces of molybdenum were removed by gently heating the tungstic acid in a current of hydrochloric acid gas. The method of operation was also somewhat different from those of the earlier experimenters. The metallic tungsten used in the oxidations was obtained by the reduction of tungstic acid in a platinum crucible at a white heat, in a current of hydrogen, which was conducted through the lid of the crucible. The mean of nine results from the oxidation of the metal is 184.921 for the atomic mass of tungsten. The maximum difference in the series is 0.043. The quantities of material used varied from 0.43 to 1.08 grams.

Smith and Desi[2] weighed the water obtained in the reduction of tungstic acid, and from that calculated the atomic mass of tungsten. The mean of six determinations is 184.704. Maximum difference 0.071.

Schneider[3] made a second series of reductions and oxidations. The material used in these experiments was freed from molybdenum by gently heating the tungstic acid in a current of hydrochloric acid gas. The values obtained for the atomic mass of tungsten were as follows:

Reduction series.	Oxidation series.
184.14	184.00
183.98	183.92
183.96	184.04
Maximum difference = 0.18	Maximum difference = 0.12

The quantities of material varied from two to six grams.

Shinn[4] obtained by oxidation of metallic tungsten the following values for the atomic mass of tungsten:

184.72
184.96
184.75
185.22
Maximum difference = 0.48

[1] *Ztschr. anorg. Chem.*, **8**, 198.
[2] *Ztschr. anorg. Chem.*, **8**, 205.
[3] *J. prakt. Chem.*, **53**, 288, *1896*.
[4] Thesis, University of Pennsylvania, 1896.

The quantities of material used varied from 0.10 to 0.22 gram of metal.

A glance at the foregoing results will show a remarkable variation. The extremely high value obtained by Berzelius is supposed to be due to the presence of alkaline impurities in the material used.

The observations of Schneider, Marchand, Borch, Dumas, and Waddell are very similar. The method of operation was the same in each case, and the material used was purified with considerable care. It is difficult to account for the variations which occur throughout these results. Molybdic acid is probably the only impurity that could have contaminated the material used in the experiments. Such an impurity would probably have lowered the separate results by the same amount, and hence would not have produced the variations. The deviations between the maximum and minimum results of the different experimenters are as follows: Schneider 1.08, Marchand 0.60, Borch 1.63, Dumas 1.38, and Waddell 0.92.

The results of Riche and Bernoulli differ widely from those obtained by other experimenters. The extremely low value obtained by the former is probably due to the method. The high results obtained by Bernoulli are more difficult to explain. The material used was carefully purified. The tungstic acid used in some of the experiments was of a greenish tinge. Some have assumed that this material was incompletely oxidized, and in this way account for the high results. Bernoulli found, however, that the greenish colored oxide and the yellow oxide gave the same results when reduced. Furthermore, neither the color of the original oxide nor the state of oxidation could affect the results obtained in the reoxidations of the metal. The results obtained by the latter method are higher than those obtained in the reductions. In view of these facts, the explanation which has been offered to account for these high results is entirely unsatisfactory.

Scheibler's results on barium metatungstate show a variation of more than one unit, and it must be added that the results obtained by the determination of the barium and tungsten in this salt were still more variable and were not used by Scheibler in calculating the atomic mass of tungsten. The two short series

of results on ferrous and silver tungstates by Zettnow are reasonably concordant.

Roscoe's experiments on the same sample of material are rather interesting. The material was reduced and reoxidized several times without being removed from the porcelain boat. The maximum difference in a series of five results is one and a half units. If the method employed by Roscoe is accurate, it is difficult to account for this variation.

The most concordant series of results on the atomic mass of tungsten is that of Pennington and Smith. The value obtained is higher than that obtained by most experimenters. Schneider[1] has attempted to account for the high values obtained in these experiments but, inasmuch as these results agree very closely with those obtained by Smith and Desi and Shinn, it is useless to offer an explanation for this high value until the true atomic mass of tungsten is known with greater certainty, at least until a series of concordant results has been obtained which differs from these.

Schneider's last determinations consist of two series of results, each series containing three observations. From these two short series of reasonably concordant results, Schneider concludes that the atomic mass of tungsten may be safely considered equal to 184.00. The evidence, however, is far from satisfactory. In view of the wide variations in the earlier determinations, the number of results in these experiments is entirely too small to establish anything with certainty in regard to the true atomic mass of tungsten. This fact is shown in the work of Waddell, who made five determinations. The maximum variation in the first three observations was only 0.22, while in the series of five the variation was 0.92. The same is noticed in the work of other experimenters. And in the present investigation, consisting of more than sixty determinations, a series of five concordant results were sometimes obtained, after which considerable variation was obtained. Attention will be called to this fact again in the discussion of the following observations:

PREPARATION OF TUNGSTEN TRIOXIDE.

The material used in the first few series of determinations was

[1] *J. prakt. Chem.*, 53, 283, *1896*.

obtained from wolframite, from Zinnwald, Bohemia. The greenish-yellow oxide obtained by digesting this mineral for several days with aqua regia was washed with distilled water and afterwards dissolved in ammonium hydroxide. The solution was evaporated to crystallization and the ammonium tungstate which separated out was strongly ignited. The resulting oxide was again dissolved in ammonium hydroxide, the solution was evaporated to crystallization, and the resulting ammonium tungstate strongly ignited. The oxide thus obtained was placed in a porcelain boat in a combustion tube and gently heated in a current of hydrochloric acid gas to remove the last traces of molybdenum. The material was then reignited and placed in a large porcelain dish filled with distilled water. Ammonia gas was conducted into the water for several days, after which the supernatant liquid was siphoned off and evaporated to crystallization. The ammonium tungstate which separated out was ignited and the process repeated. The material obtained from the second crystallization was used in the first series of experiments.

REDUCTION SERIES.

Tungsten trioxide obtained by the method just described was used in these experiments. The reductions were made in a hard glass combustion tube in a current of hydrogen, which was first conducted through solutions of ammoniacal silver nitrate, potassium permanganate, alkaline lead nitrate, caustic potash, and finally through sulphuric acid and a tube containing anhydrous calcium chloride. The reduction in each case was continued for several hours at a temperature almost high enough to melt the glass tube. The porcelain boat which contained the oxide was protected from the glass tube by means of platinum foil. The weighings were made on a Troemner short-armed balance with a set of weights which had been previously calibrated. The balance is sensitive to the fortieth of a milligram. The results calculated on the basis of O = 16 are as follows:

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	1.64084	1.30100	184.05
2	1.79728	1.42550	184.044
3	2.60739	2.06788	183.98
4	4.57390	3.62890	184.33

At this point an unglazed porcelain tube was substituted for the glass tube, and the reductions that follow were continued for three hours at the highest temperature obtainable in a combustion furnace.

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.32320	2.63547	183.94
2	6.11056	4.84580	183.91
3	9.23802	7.32393	183.66

The last experiment was continued through a period of eight hours.

The first three results agree very closely and give 184.02 as a mean for the atomic mass of tungsten. The mean of the results with the glass tube is 184.10. The maximum deviation is 0.35. The mean of the results obtained with the porcelain tube is 183.84, with a maximum difference of 0.28. The maximum deviation in the whole series is 0.67.

OXIDATION SERIES.

The metal obtained in the foregoing reductions was used in these experiments. The oxidations were made in porcelain crucibles. The material was protected from particles of dust by means of a porcelain lid suspended a short distance above the crucible. The oxidation in each case was continued until there was no farther increase in weight.

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	1.70220	2.14400	184.94
2	1.37651	1.73393	184.86
3	2.05606	2.58951	185.00
4	1.10300	1.38933	184.91
5	1.85855	2.34143	184.75
6	7.28774	9.18730	184.15

The mean of the first five results of this series is 184.89. This value is almost identical with that obtained by Pennington and Smith. The mean of the whole series is 184.77. The maximum deviation is 0.85.

REDUCTION OF OXIDE OBTAINED BY THE IGNITION OF METAL.

Inasmuch as the value obtained in the oxidation series is almost a unit greater than that obtained by reduction, it was

thought advisable to make a series of reductions of the oxide obtained in the series of oxidations.

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten
1	2.02890	1.61071	184.88
2	2.15894	1.71388	184.85
3	2.35206	1.86740	184.94
4	1.39137	1.10351	184.01
5	1.92125	1.52487	184.66
6	1.46746	1.16383	183.99
7	5.01313	3.97560	183.93
8	6.11056	4.84580	183.91

The first three results of this series agree very closely and give 184.89 as a mean for the atomic mass of tungsten. The last three results are equally concordant and give 183.94 as the mean value. The mean of the whole series is 184.40. The maximum deviation is 1.03. The oxide used in these experiments was very light and fluffy. The material used in the last experiment was moistened and re-ignited to render it more compact.

OXIDATION OF METAL OBTAINED FROM THE SECOND REDUCTION.

The material obtained in the last series was used in these experiments.

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	3.96360	4.99460	184.53
2	2.63034	3.31647	184.01
3	1.60964	2.02804	184.65

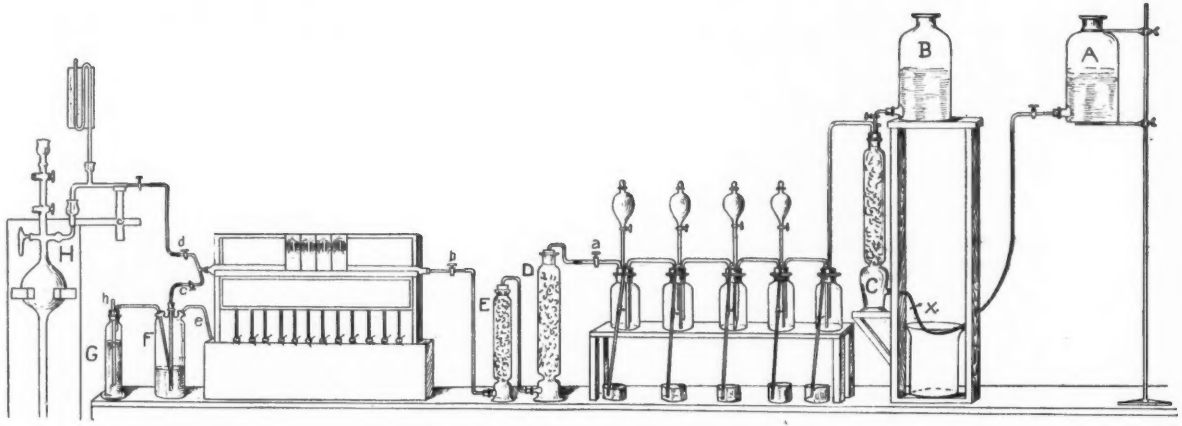
The variations in this series are similar in every respect to those of the preceding series.

In view of the wide variations in all the preceding work, an attempt was made to weigh the water formed in the reduction of tungsten trioxide. The moisture was collected in a small glass-stoppered U-tube filled with anhydrous calcium chloride. To this tube was attached another similar tube to prevent absorption of moisture from the air. Several determinations were made but the results were too discordant to establish anything. The removal of the last traces of air from the generator and wash-bottles was very difficult to accomplish, and hence the results were usually too high. The presence of air even in

small quantities would also affect the results in the reduction series. To overcome this difficulty, a different form of apparatus was constructed, the plan of which is shown in the accompanying sketch.

At the beginning of the operation, water, which had recently been boiled, was allowed to pass from the bottle *A* into the tower *C*, containing granulated zinc. When *C* was completely filled, the water passed through the small outlet tube into the first wash-bottle; after filling this it passed into the second, and so on. When the water reached the bottom of the cork in the last wash-bottle, the stop-cock at *a* was closed. The stop-cock in each of the separatory funnels was then opened and the water allowed to rise until the stems of the funnels were completely filled. In this way the air in the generator and wash-bottles was completely displaced by water. The stop-cock at the bottle *A* was now closed and sulphuric acid allowed to drop from the bottle *B* upon the zinc in *C*, the clip at *x* being opened at the same time. The hydrogen formed by the sulphuric acid and zinc, forced the water out of *C* into the beaker below, after which the clip at *x* was closed and the clip on the siphon of the first wash-bottle opened. When the water was removed from this bottle, the clip was closed and that of the second siphon opened and so on until the water in all these bottles was displaced by hydrogen. The separatory funnels were then filled with the different solutions used in purifying the hydrogen. The stop-cocks at *a*, *b*, and *c* were opened, while that at *d* was closed; this allowed the hydrogen to pass through the apparatus. The stop-cocks of the different separatory funnels were then opened and the solutions allowed to pass into the corresponding wash-bottles. The first bottle contained pure water, the second ammoniacal silver nitrate, the third and fourth potassium permanganate, and the fifth alkaline lead nitrate. The drying tower *D* was filled with anhydrous calcium chloride and caustic potash, and the tower *E* with alternate layers of glass wool and phosphorus pentoxide. These were substituted for sulphuric acid for, according to Dittmar and Henderson,[1] hydrogen when passed through sulphuric acid becomes contaminated, owing to the reduction of the acid by the hydrogen. From the drying

[1] *Proc. Phil. Soc.*, (Glasgow).


A
B
C
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G
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towers the hydrogen passed into a thin-walled, glazed porcelain tube, placed in a combustion furnace. The bottles *G* and *F* acted as a regulator; the outlet to *F* was connected to a suction tube *e*. When the suction was greater than the backward pressure of the wash-bottles, air passed in at *h* and through the columns of sulphuric acid in *G* and *F*. The length of these two columns of acid were adjusted so that the pressure exerted against the air passing through them was equal to the backward pressure of the wash-bottles. The Sprengel pump *H* was attached so that the metal might be cooled in a vacuum and thus prevent any occlusion of hydrogen. When the reductions were complete the stop-cocks at *b* and *c* were closed. The reservoir of the vacuum pump was exhausted and the stop-cock at *d* opened. This was repeated several times, until the vacuum was almost perfect.

This form of apparatus was used in all the reductions which followed. The air could be completely removed from the apparatus in a short time. The reductions were continued for a period of three hours at the highest temperature obtainable in a combustion furnace. When the quantity of material exceeded three grams the time was longer.

REDUCTION SERIES.

All the material resulting from the preceding experiments was ignited and digested for several days with pure aqueous ammonia. A residue was left, which gave the bead test for silica. It is evident from this, that tungstic acid, when reduced in a porcelain boat, takes up silica. The solution of ammonium tungstate was siphoned off and evaporated to crystallization. The crystals of ammonium tungstate were strongly ignited, and the resulting oxide used in the experiments. For the first time the metal was allowed to cool in a vacuum.

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten
1	3.55192	2.81560	183.55
2	4.59362	3.64461	184.34
3	4.30435	3.41459	184.21
4	2.64671	2.09900	183.95

The mean of these four results is 184.01. The maximum difference is 0.79.

OXIDATION SERIES.

The metal obtained in the preceding series of results was re-oxidized, and the following values obtained for the atomic mass of tungsten :

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	2.80958	3.54370	183.70
2	3.63095	4.57662	184.30
3	2.09740	2.64455	183.99

This series, like the preceding, is of little value, owing to the wide variation in the results.

Inasmuch as the removal of air from the present form of apparatus was a matter of little difficulty, another attempt was made to collect the water formed in the reduction of tungsten trioxide, and from its weight calculate the atomic mass of tungsten. The moisture was collected in a glass-stoppered U-tube filled with alternate layers of glass wool and phosphorus pentoxide. From a series of blank experiments, it seemed that any error introduced by the presence of air in the apparatus would be almost inappreciable. The following results were obtained :

	Weight of WO_3. Grams.	Weight of H_2O. Grams.	Atomic mass of tungsten.
1	5.01313	1.16742	184.07
2	2.02890	0.47090	184.86
3	7.04192	1.63864	184.27
4	3.34204	0.77832	184.07

The variations in this series are similar in every respect to those of the different reduction and oxidation series.

The next line of investigation was to make a number of determinations with material obtained from different minerals and different localities.

REDUCTION OF TUNGSTEN TRIOXIDE OBTAINED FROM SCHEELITE FROM NEW ZEALAND.

The oxide was extracted from this mineral and purified in a manner similar to that described under wolframite. No trace of molybdenum was found even before the oxide was heated in hydrochloric acid gas. The results of seven reductions are as follows :

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.41018	2.70410	183.83
2	2.99000	2.37084	183.80
3	3.11613	2.47047	183.67
4	4.32830	3.43118	183.56
5	4.66735	3.70050	183.72
6	4.29620	3.40623	183.71
7	3.39104	2.68885	183.80
8	2.93215	2.32515	183.87

The mean of this series is 183.745. The maximum deviation is 0.20. Considering the number of experiments, this is the most concordant series of results ever obtained by reducing the trioxide of tungsten and weighing the resulting metal. In experiments 2 and 7, the metal was cooled in a vacuum; in all the other experiments it was cooled in hydrogen.

OXIDATION SERIES.

The metal obtained in the preceding reductions was used in these oxidations. The results of six experiments are as follows:

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	2.70219	3.40775	183.83
2	2.36771	2.98620	183.75
3	2.46705	3.11016	184.13
4	3.42163	4.31472	183.90
5	3.40086	4.28890	183.82
6	2.68249	3.38145	184.20

This series gives a mean of 183.94, with a maximum difference of 0.45.

REDUCTION OF TUNGSTEN TRIOXIDE OBTAINED FROM WOLFRAMITE FROM CONNECTICUT.

The oxide was obtained from this mineral and purified by the method already described. The details of the work were the same as in similar series which precede. The results were as follows:

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.14520	2.49330	183.58
2	3.10516	2.46141	183.51
3	4.17792	3.31244	183.83

Mean = 183.64

Maximum difference = 0.32

OXIDATION SERIES.

The metal was obtained from the preceding reactions.

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	2.48088	3.12790	184.05
2	2.44588	3.08318	184.22
3	3.29370	4.15260	184.06

The mean of these results is almost one-half a unit greater than the mean of the reduction series. It seems that the results from oxidations are invariably higher than those obtained by reduction.

EXPERIMENTS ON MATERIAL OBTAINED FROM HUBNERITE FROM COLORADO.

The usual method of purification was used. Two reductions of the trioxide gave the following results:

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	1.83600	1.45618	184.03
2	4.31878	3.42450	183.81

The metal resulting from these reductions was reoxidized.

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	1.45184	1.83090	183.85
2	3.40470	4.29225	184.14

EXPERIMENTS ON MATERIAL OBTAINED FROM SCHEELITE FROM BOHEMIA.

The oxide was extracted and purified by the usual method. Two reductions were as follows:

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	2.77363	2.19950	183.89
2	2.13327	1.69120	183.63

The reoxidation gave:

	Weight of W. Grams.	Weight of WO_3. Grams.	Atomic mass of tungsten.
1	2.18985	2.76060	184.17
2	1.68208	2.12070	184.08

Throughout this work, it had been noticed when tungsten trioxide was heated in a current of hydrochloric acid gas for some time that a considerable sublimate was formed, even when

molybdic acid was absent. Enough of this sublimate for an atomic mass determination was obtained as follows: Tungsten trioxide was heated for some time in a current of hydrochloric acid gas at a temperature of about 400°. The sublimate was removed from the tube, strongly ignited, and gently reheated in a current of hydrochloric acid gas. The small white sublimate formed did not respond to the test for molybdic acid. The portion left in the porcelain boat was removed from the tube and strongly ignited in the air for a period of ten hours. It was then reduced in a current of hydrogen and the following result obtained:

	Weight of WO_3. Grams.	Weight of W. Grams.	Atomic mass of tungsten.
I	1.12970	0.89610	184.13

Upon reoxidation, this metal gave 184.87 for the atomic mass of tungsten.

The results from the sixty-four determinations made in the present investigation, show a maximum deviation of one and a half units. A discussion of these results, with a view of arriving at the true atomic mass of tungsten, would be useless. To take the mean of all the results would be entirely unsatisfactory, and yet there seems to be no reason why any one result should be accepted in preference to any other. It will be noticed, in several instances, that three or four consecutive results agree very closely. These different series of concordant results, however, do not agree. The variations in these results are similar in every respect to those in the results of earlier experiments.

Various causes suggest themselves as possible factors in producing these variations. The lower values obtained in the latter part of the investigation are undoubtedly due to a better form of apparatus and a higher temperature.

The reductions were all made in a porcelain boat. During each determination the boat increased in weight by from one to three milligrams. It is difficult to determine whether this absorption of tungsten by the boat would affect the results or not. If the tungsten is absorbed as metal it would produce no effect on the results, if not absorbed as metal it would. It was shown in the first part of this investigation that the metal obtained in the reductions contained silica. This may, in part,

account for the higher values obtained in the oxidations. In view of these objections to the use of porcelain, a series of reductions were made in which a platinum boat was used. This, however, did not remove the difficulty; platinum absorbs tungsten and tungsten absorbs platinum, and the results obtained were just as variable as those obtained with the porcelain boat.

A series of observations on tungsten trioxide was next made with a view of determining whether or not this compound is suitable for atomic mass determinations.

The first point was to determine how rapidly this compound takes up moisture from the air. Several series of observations were made, and it was found in each case that the absorption of water was inappreciable. The rate at which the water was absorbed is best shown by the following series of weighings of tungsten trioxide, which had been left for several days in the open air. The oxide was first strongly ignited, then placed in a porcelain boat, carefully protected from dust, and left for four days in an open window.

	Grams.
Weight of the oxide at the beginning	5.34600
" after one day	5.34605
" " two days	5.34620
" " three days	5.34625
" " four days	5.34630

From these observations it is evident that no appreciable error can be introduced by the absorption of moisture during the weighing of this compound.

A series of observations was also made to ascertain the action of light on this oxide. A weighed quantity of the material was placed in a desiccator and left for some time in direct sunlight. Weighings made at different intervals showed that no reduction had taken place. In working with this compound, it is unnecessary to cover the desiccator with a black cloth.

Upon examining the porcelain tube after a reduction, a slight sublimate was usually noticed. Whether the tungsten trioxide is volatile at that temperature, or whether the moisture formed in the reduction carried mechanically small particles of the oxide from the boat, was not determined. In either case an error is introduced, but in all probability a very small one.

A series of observations was next made to determine whether

or not tungsten trioxide contains nitrogen. A number of reductions were made in the usual way and the products set free were conducted through a U-tube containing pure water and a few drops of Nessler's reagent. The oxide used was obtained by strongly igniting ammonium tungstate for two days. Hydrogen was allowed to pass through the reduction apparatus for some time in order to completely remove the air. When the reduction was started, the solution in the U-tube began to assume a yellowish color, even when the temperature was comparatively low. Before the reduction was half completed, the solution was of a deep yellowish brown color. In some instances a slight precipitate was formed at the surface of the solution. Several observations were made, and the ammonium test distinctly obtained in each case. A series of blank experiments were made and no coloration was produced. The experiments proved conclusively that the oxide obtained by the ignition of ammonium tungstate contains nitrogen. No attempt was made to determine the quantity of nitrogen present. The oxide obtained by the ignition of metal was also examined and found to contain a trace of nitrogen. Whether the nitrogen in the former oxide was present as an oxynitride or as an ammonium residue, was not determined. If it exists as an ammonium residue, then hydrogen must also be present. A number of experiments were made by fusing the oxide with lead oxide and also with anhydrous sodium carbonate, with a view of converting any hydrogen present into water. Nothing definite was established, but there were some indications that a small quantity of water was formed. If the nitrogen is present in large enough quantities to affect the atomic mass determinations, it would probably lower the results and also produce variations, for it is not likely that the quantity would be the same in all cases.

In regard to the occlusion of hydrogen by the metal, nothing definite was established. The results obtained by cooling the metal in a vacuum were practically the same as those obtained when the metal was cooled in hydrogen.

It has been shown in the foregoing observations, that tungsten attacks the vessels in which the atomic mass determinations have been made, that the oxidation of tungsten is either slightly volatile, or that a small portion is carried mechanically by the

water formed in the reductions, and that the supposed trioxide of tungsten contains nitrogen and probably hydrogen. In view of these facts and of the fact that there is no means of determining when the reduction of oxide to metal is complete, and finally, in view of the fact that more than one hundred and fifty determinations have been made of this oxide, and nothing definite established, it is evident that the method usually employed in the determination of the atomic mass of tungsten must be regarded as unsatisfactory.

UNIVERSITY OF PENNSYLVANIA.

OBITUARY.

Mr. CARL H. SCHULTZ was born at Jutroschin-on-the-Orla, in the Province of Posen, on the 2nd of October, 1827. He began his education at the schools of his native town. In 1840 he entered the schools at Krotochin, and later the gymnasium of Lissa. From there he went to the University of Breslau, from which he graduated in 1849. Being particularly fond of chemistry and natural philosophy, he continued the study of these branches for some time after the regular course was finished.

While in the tertiary course in the gymnasium, although only thirteen years of age, he gave private instructions in mathematics and later in chemistry.

In 1853, during the World's Fair in New York, he came to America, bringing with him very little money, but some strong letters of recommendation, and was not long in finding employment. His first situation was with the late Professor Benjamin Silliman, who had charge of the Chemical Department of the Exposition. Later he was appointed assistant to Dr. John Torrey, Professor of Chemistry at the College of Physicians and Surgeons, then in Crosby street. In 1854 the United States Assay Office appointed Dr. Torrey Chief Assayer, and he at once made Mr. Schultz his assistant. He not being a citizen of the United States was offered as an objection to his appointment, but he overcame this by taking out his first papers, and after the proper time, his second papers. Few men ever felt prouder of their citizenship or could have been more thoroughly American.

While at the Assay Office, besides his routine work of making

gold and silver assays, he found time to do a good deal of investigation in connection with Dr. Torrey, and much valuable work toward improving the methods of assaying. At the same time he did the chemical work for the Manhattan Gas Company,

and the laboratory at 18th Street Station was fitted up under his supervision, and remains to-day, with few alterations, as he left it.

While holding the position at the Medical College in Crosby Street, he lodged in the college building and took his meals in a boarding house in the neighborhood. There he met the late

Thomas Warker, who showed him a French siphon. With his characteristic quickness of perception, he at once saw its advantages for keeping water fresh and sparkling, and especially its value in the sick-room. Believing that the manufacture of artificial mineral waters would be a profitable industry, he began making investigations on the subject.

In 1862 he and Thomas Warker established a business for the production of mineral waters on a small scale, under the firm name of Schultz and Warker, which continued until 1871, when Mr. Schultz bought out Mr. Warker's interest, and has since conducted the business under his own name. In 1871 the business had assumed such proportions that it was necessary to move into larger quarters, and he purchased property on First Avenue and located his factory where the business is still continued.

In 1867 he was sent to Europe to examine into the methods of assaying employed by foreign governments, and on his return he submitted a report, many of the recommendations of which were adopted.

In 1872, after seventeen years of service, he resigned from the Assay Office and also from the Manhattan Gas Co., although he was afterwards many times called upon in consultation in regard to questions of great importance. General Roome, President of the Gas Co., once remarked that Dr. Schultz's opinion was of special value to them, because it carried with it not only thorough scientific knowledge, but sound business judgment as well, and no matter how much pressure was brought to bear upon him, he would not endorse anything until satisfied by investigation of its merit.

As an illustration of his untiring industry and genius for application, I might mention, that for a number of years after establishing his business, he still retained his position in the Assay Office and remained chemist to the Gas Co., any one of which posts would be regarded by many men as quite sufficient for the employment of all their energies.

He was very fond of chemical work, and often regretted that he had not more time to devote to it, and those who have visited the factory, will agree with me that his laboratory is the finest and best equipped in the country. It was fitted up without the slightest regard to expense, and with no restrictions

whatever on apparatus or supplies. What a boon it would be to our profession if more of our employers took so much interest in science and provided their chemists with every facility for work.

He was a genial and companiable man, cordial and friendly to all to a degree seldom met with. Especially marked was his consideration and sympathy for those in his employ. His men came to feel that in him they had a good and true friend who would not forsake them, a feeling justified by his many benefactions.

Naturally of a charitable disposition, he not only contributed liberally to public charities, but his private benefactions were both numerous and judicious. Many a man would never have attained the position he now holds, had it not been for Mr. Schultz's timely assistance.

The most lovable side of the man was best seen in his home and in his social relations. He and his wife were most genial hosts and most lavish entertainers when they resided in 140th street, and later at their beautiful home in Murray Hill. He leaves a wife, ten children and seven grandchildren to mourn his loss. The funeral was held at his late residence in Murray Hill on May 31st. The interment was in Long Hill Cemetery, near Summit, about three miles from his home.

Mr. Schultz was a member of the American Chemical Society, New York Academy of Sciences, the College of Pharmacy, the American Association for the Advancement of Science, the Reform Club, and all the prominent German Clubs in this city.

Mr. Schultz was a man of keen insight, sound judgment, and affectionate and generous disposition. To be counted among his friends was an honor and a privilege. A. P. HALLOCK.

NOTE.

Hydrolysis of Starch by Acids.[1]—*An Apology.*—It has recently been brought to our notice that in 1880 and 1881[2] Prof. H. W. Wiley demonstrated that a practically constant relation existed between the optical and copper-reducing constants in samples of commercial glucoses investigated by him. We wish to apolo-

[1] This Journal, **18**, 869, 900.

[2] Proc. Am. Assoc. of Sci., *1880* and *1881*.

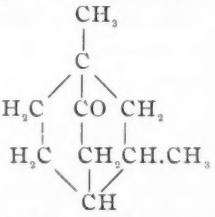
gize to Prof. Wiley for our neglect to refer to his work, and state that the unintentional omission was made because the presumably complete bibliographies consulted by us made no mention of these papers.

GEO. W. ROLFE,
GEO. DEFREN.

NEW BOOKS.

TRAITÉ DE CHEMIE ORGANIQUE D' APRÈS LES THÉORIES MODERNES. By A. BEHAL. Tome Second. pp. 1056. Paris: Octave Doin. Price 17 francs.

The general merits and excellencies of this work were pointed out in the review of the first volume;[1] these are maintained in the present and concluding portion. A clear demonstration of the structure of benzene is first given, so far as the presence of a closed chain and the number and nature of isomeric derivatives are concerned. Of the various expressions which have been suggested for its representation, Kekulé's is, after discussion, preferred. The section dealing with cyclopolymethylenes comprises 125 pages, of which 80 are devoted to the terpenes; this portion is fully equal to the high expectations inspired by the author's investigations in this field. The formula



is provisionally assigned to camphor for reasons given. It would have been well to have also shown Bredt's formula as a possible alternative. V. Baeyer's system of nomenclature is employed in this section, and also his plan of distinguishing isomers. In connection with the benzaldoximes, Hantzsch and Werner's theory of stereoisomerism is examined in detail and rejected on the following grounds: (1) It indicates the existence of stereoisomeric derivatives of trivalent nitrogen atoms, such as $C_6H_5CH:NC_6H_5$, which are unknown in spite of special efforts to obtain them. (2) It supposes that certain radicals in the molecule may both attract and repel one another without any previous

[1] This Journal, 19, 437.

chemical changes occurring in the compound. (3) It does not accord with the formation of two isomeric derivatives by the introduction of a radical into the molecule of β-benzaldoxime, although such compounds are known. The author represents α-benzaldoxime by the ordinary formula $C_6H_5.CH:NOH$, and the β compounds by one or other of the formulas $C_6H_5.CH\underset{O}{\diagdown\!\diagup}NH$; $C_6H_5.CH{:}NH\overset{\|}{O}$. Possibly these conclusions explain the absence of reference to Hantzsch's extension of his conception of stereoisomerism to diazo compounds, and of his controversy with Bamberger on the constitution of these and similar substances. As in the first volume, so in this, there are certain omissions which are difficult to understand, and which it would appear hard to justify; for example, Claisen's name is not recorded in connection with the isoxazoles, nor is reference made to his work and Nef's on the constitution of di- and triketones, such as dibenzoylmethane and tribenzoylmethane, which are simply represented by the keto formulas, nor is the isomerism which has been observed in this series of compounds mentioned. The alkaloids are classified according to the plant from which they orignate; in the present state of our knowledge this is decidedly commendable, but the omission of W. Kœnig's name in connection with the quinine group, and of Schunk's in connection with chlorophyll, is scarcely equitable, whilst A. G. Perkin's investigations of the constitution of natural coloring matters has not been confined to mallotoxin (rottlérine), as might be inferred. The "salt formation" is given in explanation of the action of phenol phthaleïn as an indicator. The electrolytic dissociation theory offers a much more probable solution of the phenomena. The volume concludes with a copious index to both parts of the work.

J. B. T.

BOOKS RECEIVED.

Commercial Fertilizers. Special Bulletin, May, 1897. H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. 8 pp.

1. General Discussion on Commercial Fertilizers. 2. Analyses of Fertilizing Materials sent on for Examination. 3. New Fertilizer Law.

Bulletin No. 45, March, 1897. 16 pp. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

The Habits, Food, and Economic Value of the American Toad. Bulletin No. 46, April, 1897. 30 pp. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

On Field Experiments with Tobacco in Massachusetts. Bulletin No. 47, April, 1897. 31 pp. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass.

A Handbook on Modern Explosives. By M. Eissler. Second edition, enlarged. 150 illustrations. xx + 406 pp. London: Crosby, Lockwood & Son; and New York: D. Van Nostrand Co. Price, $5.00.

The San José Scale in Kentucky. Bulletin No. 67. 17 pp.; Analyses of Commercial Fertilizers. Bulletin No. 68. 13 pp. May, 1897. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

Twentieth Annual Report of the Connecticut Agricultural Experiment Station for 1896. Agricultural Experiment Station, New Haven, Conn. xvi + 414 pp. Report of Station Staff on Food Products; Their manufacture and sale; Maple syrup and maple sugar; Sugars; Syrup; Honey; Lard; Pepper; Mustard; Cheese; Coffee; Milk; Cream of tartar, and cereal foods, and laws regulating foods and drugs; Fertilizers; Connecticut fertilizer law; Sampling; Miscellaneous analyses and reports; Availability of nitrogen; Experiments with forcing house crops, tomatoes, radishes, carnations, and cucumbers; Blight, burn or scald of tomato plants; Insect notes; Prevention of potato scab; Leaf blight of melons; Fungus of peach scab; Shelling of grapes; Experiments in growing tobacco with different fertilizers; Nitrogen, phosphoric acid and potash in peas and beans; Observation on the growth of maize continuously on the same land for nine years; Effects of minute quantities of acid on the solubility of globulin in salt solutions; Proteids of lupin seeds; Sunflower seeds; Cow pea; White podded adzuki bean, and maize kernel.

An Electrical Method of Determining the Moisture Content of Arable Soils. By Milton Whitney, Frank D. Gardner, and Lyman J. Briggs. Bulletin No. 6, U. S. Department of Agriculture, Division of Soils. 26 pp. Washington: Government Printing Office.

The Chlorination Process. By E. B. Wilson, E.M. v + 125 pp. New York: John Wiley & Sons. Price, $1.50.

ERRATA.

Page 552 (July number), line 12, for "zinc ammonium sulphate" read "zinc ammonium phosphate."

Page 587 (July number), line 3 from bottom, for "+" read "—."